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ABSTRACT

This booklet is designed to supplement the study of introductory chemistry. It deals particularly with the mole concept but also includes ideas for analyzing the kinds of statements that appear in all science textbooks and scientific writing. The material in the booklet should be studied after the completion of an introductory textbook study of the mole concept. Part 1 presents an analysis of the mole concept and part 2 is an account of the contributions of Dalton, Gay-Lussac, and Avagadro to the mole concept. The main text appears only on odd-numbered pages; the even-numbered pages contain corresponding commentaries and suggestions for analyzing the text. (MH)

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THE MOLE AS AN EXPLANATORY DEVICE: HOW DO YOU KNOW A MOLE IF YOU SEE ONE?

A MANUAL FOR CHEMISTRY STUDENTS

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Sample Teaching Materials

THE EXPLANATORY MODES PROJECT

Douglas A. Roberts, Principal Investigator

Developed in Collaboration with The Science Department, Thornlea Secondary School, Thornhill, Ontario

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THE MOLE AS AN EXPLANATORY DEVICE:
How Do You Know a Mole if You See One?

A Manual for Chemistry Students

written by
Douglas A. Roberts

with the assistance of
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and
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Sample Teaching Materials
THE EXPLANATORY MODES PROJECT
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A NOTE TO THE STUDENT . . .

This booklet is designed to supplement your study of introductory chemistry. It deals especially with the mole concept, but the ideas in it are useful also for making sense out of the kinds of statements which appear in all science textbooks and scientific writing. It will introduce you to ways to identify different kinds of statements, and also different ways to establish the truth of statements in science. To do this, we have drawn on a specialized branch of philosophy known as "analytic philosophy." We are analyzing kinds of statements.

The booklet is to be studied after you have completed an introductory textbook study of the mole concept. It is keyed to two textbooks in particular, Chemistry: An Experimental Science[1], and Chemistry: Experiments and Principles[2]. If you are using either of these two textbooks, this booklet should be studied after completion of your study of Chapter 2.

Turn now to page 3, and notice that the "story" of the booklet continues from page 1 to page 3 (not page 2). The booklet is deliberately set up this way, so the "story" appears only on the odd-numbered pages. Notice, then, when you get a short way down page 3, you are stopped by the words *"BEFORE YOU READ FURTHER . . .* Study COMMENTARY #1 on page 2 (facing this page.)" There are many such COMMENTARIES in the booklet, and they appear on the even-numbered pages. They must be studied at the point where you are instructed to study them--not before, and not after. Otherwise, the story of the booklet will not communicate clearly to you.

The booklet has two parts. PART 1 presents an analysis of the mole concept as we now understand it. PART 2 is an account of three major contributions to the development of the mole concept, and analyzes some aspects of work done in the early 1800's by the chemists Dalton, Gay-Lussac, and Avogadro.

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[1]George C. Pimentel, ed., Chemistry: An Experimental Science, prepared by the Chemical Education Material Study (San Francisco: W. H. Freeman and Co., 1963).

[2]P. R. O'Connor et al., Chemistry: Experiments and Principles (Toronto: Copp Clark Publishing Co., 1968; also, Lexington, Mass.: D. C. Heath and Co., 1968).

PART 1. AN ANALYSIS OF THE MOLE CONCEPT

This booklet is about moles. Not the little animals (*Scalopus aquaticus*, to a biologist) that burrow around under the lawn. If you observed one of those, you would probably recognize it when you saw it. And you would probably be rather confident in saying you knew it was a mole, rather than a rat, or a squirrel, or a porcupine.

But how can you recognize a mole of the kind you study and use in chemistry? For instance, how does someone know how many moles of copper he has deposited, in an electroplating experiment?

1.1. Did Someone *Really* Count All Those Particles?

One widely used secondary school chemistry textbook provides the following information about a mole.[1]

> We never work with individual atoms or molecules but always with collections of these particles. Chemists, therefore, have selected a unit larger than a single atom or molecule for comparing amounts of different materials. This unit, called the mole, contains a very large number of particles, 6.02×10^{23}. A mole of oxygen atoms, a mole of hydrogen atoms, or a mole of copper atoms contains 6.02×10^{23} atoms of the specified kind.

This passage suggests that our experimenter could know how many moles of copper he deposited by counting the atoms of copper, and then dividing his result by 6.02×10^{23}.

Of course, the text passage does not say that you recognize a mole (or part of a mole) by counting particles. But it is easy to read this passage as if it were written in "everyday language," as if the word "mole" were being used in the same way as a word like "dozen." The word "dozen" means "twelve." The two words are completely interchangeable in everyday language. Had you read the text passage as if it were in everyday language, you would conclude that the word "mole" means "602,000,000,000,000,000,000,000" and nothing else, like "dozen" means "12" and nothing else. You would understand the word "mole" as a "convenient counting word" which could refer to a collection of 602,000,000,000,000,000,000,000 of anything--say, a mole of pencils, or a mole of sand grains. That understanding would be incorrect.

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[1] Pimentel, op. cit., p. 32. A similar passage appears on page 31 of O'Connor et al., op. cit.

COMMENTARY #1

When you are reading a passage of scientific writing, it is easy to miss key words and phrases, and other clues, which make the difference between understanding the passage and misinterpreting it. (This is a general problem when people try to communicate, of course. It is not limited to scientific writing. People always use clues to communicate, and to understand, the context in which statements are supposed to make sense.)

In the quotation on page 1, there are two clues which signal the reader that it is very important not to interpret the definition of "mole" in everyday language. The purpose of this COMMENTARY is to show how the two clues operate in the communication process, and thus to increase your awareness of the way clues indicate contexts, especially in scientific writing.

The first clue we wish to emphasize is a key phrase in the second sentence: for comparing amounts of different materials. This clue alerts us that the unit being discussed (the mole) is a comparing device, not a counting device, and that it is applicable to different materials in chemistry. Reread that second sentence now, with this clue in mind, and *notice how the clue steers you away from thinking about a mole of anything except a chemical substance.* You are alerted that "mole" is a highly technical term, and it is rather dubious that it would be used in the same way as an everyday word like "dozen."

The second clue reinforces the first. It appears in the third and fourth sentences. The unit called a "mole" (already clued as a technical term, not an "everyday" term) is said to contain 6.02×10^{23} particles, *and the only examples mentioned are atoms.* A mole of oxygen atoms, or hydrogen atoms, or copper atoms: all are said to contain the same number of atoms.

These two clues form the basis for talking about two important differences between the word "mole" and everyday "convenient counting words" like "dozen." They will be taken up in the following sections of the booklet.

COMMENTARY #2

A *postulated entity* is an imagined thing, which is "thought up" for the purpose of developing an explanation for something which occurs (let us refer to something which occurs as a *states-of-affairs event*.) For example, a frightened child might postulate a "boogeyman" as the entity which is causing the window-blind to rattle in his bedroom at night. (The explanation might be, "The boogeyman is trying to get in to get me.") One parent or the other arrives, adjusts the blind, and explains to the child, "It was only the wind." Let us refer to something like "the wind" as an everyday object, or a *states-of-affairs object*. It doesn't have to be imagined, or postulated, because we have ample *states-of-affairs* experience with it.

In science, postulated entities, such as atom, electron, molecule, etc., resemble "the boogeyman" in only one respect. At the time they were suggested for purposes of explaining *states-of-affairs events*, they were imagined, not experienced directly. They are theoretical in nature, and any statements made about them are theoretical also.

We will discuss *postulated entities*, and *theoretical statements* about them, in more detail. For now, it is sufficient to note that *postulated entities* (or "imagined things") are very different from *states-of-affairs objects* ("things" with which we have direct experience).

To see why, we need to examine the built-in clues which show that an "everyday language" interpretation of the text passage is not appropriate.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #1 on page 2 (facing this page). Let's have a look at these "built-in clues."

1.2. Never a Mole of Pine Needles

THE WORD "MOLE" IS NOT A "CONVENIENT COUNTING WORD" LIKE "DOZEN." It is different in two important ways.

The first difference we'll examine has to do with the kinds of objects to which each word can properly refer. The word "mole" cannot properly be used to refer to just any collection of 602,000,000,000,000,000,000,000 objects. (But notice that the word "dozen" can properly be used to refer to any collection of 12 objects.)

It's difficult to imagine encountering very many collections of 602,000,000,000,000,000,000,000 objects. But suppose you did. Suppose that, for some reason, it was important to know the number of needles on all the live pine trees of every kind in Canada. And suppose further (as unlikely as it seems) that the number was exactly 602,000,000,000,000,000,000,000. It would NOT be proper to speak of that number of pine needles as a "mole of pine needles."

Why not? In COMMENTARY #1 it was pointed out that "mole" is a technical term. The text passage quoted on page 1 specifies only one kind of example to which "mole" is applied: atoms.

Atoms are not "everyday objects" in the same sense as pine needles, or pencils, or sand grains. Instead, they are what we might call "scientific objects." Such "scientific objects" as atoms, molecules, electrons, protons, neutrons, ions, etc., were not seen first and named later, in the way "everyday objects" normally are. They originated in people's minds, and are referred to technically as *postulated entities*.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #2 on page 2 (facing this page). A *postulated entity* is different from an "everyday object," which we will call a *states-of-affairs object*.

COMMENTARY #3

The use of *postulated entities* is very common in the development of scientific theories and is especially important in atomic-molecular theory. As you know, the usefulness of a theory is that it enables a person to explain "what's happening out there in the world." That is, a theory is an explanation for *states-of-affairs events and objects*: how it is that events occur as they do, and how objects came to be as they are.

But the statements of atomic-molecular theory do not consist of direct reports about states-of-affairs events and objects. Rather, the statements report what has to be thought to be happening to the postulated entities of the theory, if one is to be able to explain the observable states-of-affairs events.

So, to talk about postulated entities is to use language in a different way from the way we use everyday language in talking about states-of-affairs. You have to shift from the "observable realm" to the "explanatory realm." (That's why we refer to the mole as an "explanatory device." It is in the explanatory realm, where you have to think of what is happening to postulated entities. It is not in the observable realm, where you can point to objects and count them.)

Any reference to a number of postulated entities, therefore, has to be in the explanatory realm as well. That is, we are not using the language in the same way when we speak of a number of postulated entities, as we are when we speak of a number of states-of-affairs objects. (This point will be taken up in more detail in COMMENTARY #6.) We have to be speaking of a *theoretical number*, which doesn't mean the number has been "made up" on fictitious grounds, but means that it is calculated carefully from *theoretical considerations* about what is happening to postulated entities. It is a number in the explanatory realm.

Test your understanding of the difference between language in the observable realm and the explanatory realm, with this example. Suppose someone asks, "How is it that gases expand when they are warmed?" The reply could properly be, "The molecules gain kinetic energy from the heat applied to the gas, and therefore move faster, collide harder, and move further apart as a result of their collisions."

Where did the shift in language take place? Which statements are in the observable realm, and which are in the explanatory realm? (Notice how important it was to use a clue so that you would know the context of the statements, as discussed in COMMENTARY #1. The clue, in this case, is the use of the word "molecules"--a molecule is a postulated entity.)

Optional Further Reading

1. Stephen Toulmin's book The Philosophy of Science: An Introduction contains an excellent, and quite readable account of the shift in language necessary to move from the observable realm to the explanatory realm in science. It is found in Chapter II of the book. (It is a paperback, published by Harper and Row in 1960 as a "Harper Torchbook," #TB513.)
2. Ernest Nagel's book The Structure of Science: Problems in the Logic of Scientific Explanation contains a technical, but clear discussion of postulated entities in Chapter VI, pp. 106-152. (The book is published by Harcourt, Brace, and World, Inc., 1961.)

From COMMENTARY #2, we note that statements about a number of *postulated entities* are statements about a *theoretical number* which has been calculated from *other theoretical statements*. Someone who talks about a number of directly observable "everyday objects," or *"states-of-affairs" objects*, however, is talking about a number which has been counted from *states-of-affairs* experience.

It is most important to keep this distinction in mind, because it is one major reason why the word "mole" cannot be applied to a collection of 6.02×10^{23} pine needles, or other such *states-of-affairs objects*.

> THE WORD "MOLE" IS PROPERLY USED ONLY TO REFER TO A *THEORETICAL NUMBER OF POSTULATED ENTITIES* IN ATOMIC-MOLECULAR THEORY: ATOMS, MOLECULES, ELECTRONS, PROTONS, NEUTRONS, IONS, ETC.

Never a mole of *states-of-affairs objects*. Never a mole of pine needles. We will extend this discussion with an example, in the next section.

> *BEFORE YOU READ FURTHER . . .*
>
> - Study COMMENTARY #3 on page 4 (facing this page). It contains information important for understanding *postulated entities* and *theoretical numbers*.

1.3. Not Even a Mole of Sugar Granules

It has been noted, in the previous section, that the word "mole" properly refers only to a theoretical number of postulated entities from atomic-molecular theory. Let us consider one further example of proper and improper usage of the word "mole," based on a passage from the text quoted earlier. The passage[1] follows shortly after the one quoted on page 1.

> A baker counts biscuits in dozens--a convenient number. Money is counted in dollars--one hundred cents is, again, a convenient number. How did chemists choose to count in terms of moles--the number 6.02×10^{23} seems an odd choice. Why, for instance, didn't they settle on some simpler number, such as exactly one billion particles? There is a reason. Chemists prefer a definition in terms of a quantity that can be measured readily and with high accuracy. Weighing is easier than counting when the number of particles to be counted is so very large.

Notice how important it is to read this passage in the proper context, as pointed out in COMMENTARIES #1, #2, and #3. Biscuits and cents are

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[1] Pimentel, op. cit., pp. 32-33. A similar passage appears in O'Connor et al., op. cit., p. 32.

COMMENTARY #4

The history of a postulated entity always shows that it was invented for the purpose of explaining observable states-of-affairs events or objects. But it is not the invention of wild imagination; it is the invention of disciplined thought. We will pursue this point in some detail in PART 2 of this booklet, where historical accounts of the invention of some postulated entities will be given.

And there are ways in science to check on "how good" a postulated entity is, and how good all the invented (theoretical) statements about its behavior are, also. There is always a checkpoint at which a prediction is made about observable states-of-affairs (but not the same ones as those on which the postulated entity and its behavior were originally based). If the prediction is borne out in observation, then the postulated entity itself, and the theoretical statements about its behavior, are considered valid, at least for the time being.

As scientific instruments have become more sophisticated, some scientists who wonder about the actual existence of postulated entities have tried to detect them indirectly. Unfortunately, it is all too easy to interpret "indirect evidence" (see below) from sophisticated instruments as "states-of-affairs" evidence for the existence of postulated entities. This blurs the distinction between postulated entities and states-of-affairs objects, and produces potential confusion for anyone trying to understand how science operates. For example, to count the "clicks" of a discharge-tube counter, and then to claim that each represents the passage of a "real thing" identical to the original postulated entity through the tube, is to fail to realize that a language shift is needed.

Optional Further Reading

1. The textbook Chemistry: An Experimental Science (Pimentel, op. cit.) contains an excellent treatment of some of the indirect evidence about postulated entities in atomic-molecular theory, in Chapter 14, pp. 233-251. A less extensive account is given in Chemistry: Experiments and Principles (O'Connor et al., op. cit.), Chapter 8, pp. 121-139.

   You might find it interesting just to read briefly some of either or both of these chapters, being especially alert for clue words which indicate the context in which the statements are to be understood. (Refer back to COMMENTARIES #1, #2, and #3.) For instance, the first text mentioned signals the language shift necessary to understand the statements by placing in quotation marks those words which ordinarily refer to states-of-affairs operations ("seeing" electrons, "weighing" positive ions, etc.). This is a clear signal that the seeing and weighing are to be understood as interpretations of evidence, as requiring a shift from the observable realm to the explanatory realm. The second text refers, for example, to the failure of models to explain experimental data, or to the way in which particular investigators pictured the atom, etc., in order to signal that a language shift is necessary.

2. The process of checking the validity of a postulated entity, and of the theoretical statements made about its behavior, is described very well in Henry Margenau's book Open Vistas: Philosophical Perspectives of Modern Science (Yale University Press, 1961).

both what we have called "states-of-affairs objects," or everyday objects. But the particles which chemists "count in terms of moles" must be understood as postulated entities. Otherwise the meaning of the passage can be misinterpreted.

To see how this can happen, let us examine carefully the last sentence of the passage: "Weighing is easier than counting when the number of particles to be counted is so very large."

If you place an "everyday language" interpretation on that sentence, it would seem that chemists weigh particles instead of pointing at them and counting them, because they have chosen the easier of two possible ways to proceed. Thus, you might conclude (incorrectly) that a mole is used in chemistry in the same way a pound is used in selling sugar.

Sugar is sold in containers which announce the weight of sugar inside them, not the number of granules. And that is because weighing is easier than pointing and counting. The easier of two possible ways to proceed has been chosen in this case. It is possible actually to point at and count each sugar granule in a pile, and sell sugar by the million granules, for instance, even though it is unlikely anyone would have the patience to do so. The granules can be seen with a hand lens, picked up with a pair of forceps, and then pointed at and counted one by one. They are states-of-affairs objects, and so it is possible to point at them and count them.

But 6.02×10^{23} sugar granules would not properly be called a mole of sugar granules, for the same reason that 6.02×10^{23} pine needles would not properly be called a mole of pine needles. As we will see in a later section, a mole of sugar (not sugar granules) can be recognized, once the type of sugar is specified (since there are several which are distinguishable chemically). It can be recognized by weighing, but not by pointing at and counting a lot of particles. That isn't because weighing is easier than pointing and counting. *It is not possible to point at and count postulated entities*, such as molecules of whatever kind of sugar is chosen. Pointing and counting is a states-of-affairs operation performed on states-of-affairs objects. And postulated entities are not states-of-affairs objects.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #4 on page 6 (facing this page). The question of counting "states-of-affairs objects" and postulated entities is pursued there, and will be helpful for digesting this section.

COMMENTARY #5

602,000,000,000,000,000,000,000 is a large number. It is written more simply in powers-of-ten notation, as 6.02×10^{23}. In words, for the sake of anyone counting "everyday objects," it could be one of two different expressions.

In Canada, the U.S., and France, it would be 602 sextillion. In Great Britain and Germany, it would be 0.602 quadrillion. Why the difference?

Let us start with "billion." In Canada, the U.S., and France, a billion is defined as a thousand millions ($10^3 \times 10^6$, or 10^9). But in Great Britain and Germany, it is defined as a million millions ($10^6 \times 10^6$, or 10^{12}).[1]

It gets more complicated with a trillion. In the former three countries, a trillion is defined as a thousand billions ($10^3 \times 10^9$, or 10^{12}). In the latter two countries, it is defined as a million billions ($10^6 \times 10^{12}$, or 10^{18}).[2]

Using these definitions and the table below, verify for yourself that 6.02×10^{23} is 602 sextillion in Canada, the U.S., and France, while the same number is 0.602 quadrillion in Great Britain and Germany.

Number	Word Equivalent (Canada/U.S./France)	Word Equivalent (Gt. Britain/Germany)	Powers-of-ten Notation
1,000,000	1 million	1 million	10^6
1,000,000,000	1 billion (1 thousand millions: $10^3 \times 10^6$)	1 thousand millions[3] ($10^3 \times 10^6$)	10^9
1,000,000,000,000	1 trillion (1 thousand billions: $10^3 \times 10^9$)	1 billion (1 million millions: $10^6 \times 10^6$ or 1 thousand milliards: $10^3 \times 10^9$)	10^{12}
1,000,000,000,000,000	1 quadrillion (1 thousand trillions: $10^3 \times 10^{12}$)	1 thousand billions[4] ($10^3 \times 10^{12}$)	10^{15}
1,000,000,000,000,000,000	1 quintillion (1 thousand quadrillions: $10^3 \times 10^{15}$)	1 trillion (1 million billions: $10^6 \times 10^{12}$)	10^{18}
1,000,000,000,000,000,000,000	1 sextillion (1 thousand quintillions: $10^3 \times 10^{18}$)	1 thousand trillions ($10^3 \times 10^{18}$)	10^{21}
602,000,000,000,000,000,000,000			6.02×10^{23}
(What would this number be?)	1 septillion (1 thousand sextillions: $10^3 \times 10^{21}$)	1 quadrillion (1 million trillions: $10^6 \times 10^{18}$)	10^{24}

[1]See Dictionary of Canadian English: The Senior Dictionary (Toronto: W. J. Gage, Ltd., 1967), p. 112.

[2]Ibid., p. 1181.

[3]In Great Britain, there is a one-word equivalent for this number: the milliard. Note that the usual French term for the American "billion" (10^9) is *milliard*, and the German word for the same number (10^9) is *Milliarde*. (The German *Million*, like the English million and the French *million*, means 10^6.) See Webster's Third International Dictionary of the English Language Unabridged (Springfield, Mass.: G. and C. Merriam Co., Publishers, 1968), p. 1549.

[4]There is no one-word equivalent for this number, or for 10^{21}, etc., in Great Britain. See Webster's Third International Dictionary, p. 1549.

1.4. Arbitrary Choice *Versus* Theoretical Consistency

Let us return briefly to the textbook passage quoted on page 5. The third and fourth sentences suggest that chemists had a choice about whether to "settle on" a mole as 6.02×10^{23} particles, or some "simpler number" such as a billion particles. The reason given for the selection of 6.02×10^{23} is that a quantity was needed that could be measured readily--*something that could be detected reliably in states-of-affairs*, to use the distinction we have been developing.

But that measurable quantity is not a number of particles. The number 6.02×10^{23} was calculated on the basis of certain states-of-affairs measurements and theoretical statements as well. The choice of 6.02×10^{23} (rather than one billion) was not arbitrary, then. It followed from other theoretical statements, and any other number would have been logically inconsistent with the rest of atomic-molecular theory. (You might find it helpful to refer back to COMMENTARY #3 at this point. Also the importance of logical consistency between theoretical statements is demonstrated in Section 2-2.1 (pp. 22-24) of Pimentel, op. cit., and Section 2-1 (pp. 21-23) of O'Connor et al., op. cit.) *Let us refer to this logical consistency between theoretical statements as theoretical coherence.*

There would also have been some international confusion if "one billion" had been chosen as the theoretical number of particles in a mole.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #5 on page 8 (facing this page). If someone really wanted a "convenient counting word" to designate 6.02×10^{23} states-of-affairs objects, "mole" would not do. He would have to settle for the name of the number: 602 sextillion. Or would it be 0.602 quadrillion? It depends on where you live.

1.5. Recognizing a Mole

Let us now consider the second difference between a "convenient counting word" like "dozen," and the word "mole."

It will be recalled, from the preceding pages, that the kinds of objects properly referred to by the word "mole" include only postulated entities from atomic-molecular theory--that is, atoms, molecules, electrons, protons, neutrons, ions, etc. States-of-affairs objects, such as pine needles, sand grains, doughnuts, sugar granules, pencils, and oranges are not properly

COMMENTARY #6

The philosophical distinction between *analytic* and *empirical* statements is extremely useful for making sense out of what is written in science textbooks. This COMMENTARY might seem complicated, and it might put you off at first. But bear with it, and study it carefully. Your understanding of the mole will be considerably strengthened, if you do.

ANALYTIC STATEMENTS tell the meaning of words. They are definitions, and they permit people to communicate meaningfully. A dictionary is full of *analytic* statements, and each is true *because it tells how to use a word.*

So the truth of an *analytic* statement is established automatically if the statement tells how a word (or phrase) is to be used. The statement "This is a cat" is not *analytic*. But the statement "A cat is an animal having the attributes (a), (b), (c) . . . etc." is *analytic*, because it specifies the way in which we use the word "cat" (to refer to an animal with those attributes).

But *EMPIRICAL* STATEMENTS are not statements about how words are used. They are statements about "the world of objects and events." The statement "This is a cat" is an *empirical* statement. The truth of the statement is not determined by definition, but rather by (1) pointing to (looking at) the animal itself, and (2) being sure that the animal in question does in fact have the attributes of the animal to which we apply the word "cat."

Notice that it is impossible to know whether an *empirical* statement is true, unless you have an *analytic* statement to guide you. Our example about the dozen oranges shows this clearly. *Analytic* statement (a) is the basis for a sensible *empirical* statement (c), and *analytic* statement (b) is the basis for a sensible *empirical* statement (d). Young children who point to objects and ask "What is that?" are often seeking an *analytic* statement for an answer--a definition which tells them how to communicate about and refer to the object.

So far, *we have talked about only one of three possible ways for establishing the truth of empirical statements.* Philosophers distinguish three "theories of truth" for *empirical* statements. (We will call these three different "truth strategies.") The first, which we have been talking about above, with reference to the cat, is called *Correspondence Theory*. To determine the truth of the *empirical* statement "This is a cat," a "*Correspondence* strategy" is quite proper: one sees if the (observable) object corresponds to the definition. So this strategy relies on direct correspondence between definitions and states-of-affairs, as in the case of the dozen oranges given as an example on page 11.

But notice that a *Correspondence* strategy will not work for a postulated entity, since there is no observable object to point out, to see if it corresponds to the definition. The second "theory of truth" for *empirical* statements, the *Coherence Theory*, is proper for a situation of this kind. Let us see how a "*Coherence* strategy" works.

Suppose an experimenter is evacuating a glass tube filled originally with pure hydrogen, and reports to you that the pressure is down to 10^{-5} atmosphere, or 7.6×10^{-3} mm of mercury. The truth of that report could be

COMMENTARY #6 continues on page 12 . . .

referred to by the word "mole," even if you happened by unlikely circumstances to encounter a collection of 602,000,000,000,000,000,000,000 of any of these.

The reason given for this distinction is that *you cannot point to and count postulated entities, as you can do with states-of-affairs objects.* In this section, we wish to elaborate on the reasons why this is so, in somewhat more detail than is shown in COMMENTARY #3 and COMMENTARY #4. The discussion has to do with how you establish the truth of a statement such as, "I have a mole of oxygen here."

Suppose a friend said to you, "I have a dozen oranges here." How would you establish the truth of that statement? (This has nothing to do with doubting the word of friends. It has only to do with the process people use to establish and communicate the truth of statements.) Let us separate the statement into four parts, as follows.

(a) An orange *is defined as* a fruit having certain attributes, such as specific color, texture, roundness, smell, taste, etc. (So I can tell the difference between oranges and non-oranges--like lemons, kumquats, and grapefruits--by *definition* of what an orange is.)

(b) "One dozen" *is defined as* "12."

(c) I identified each object in my group as an orange, consistent with (a).

(d) I pointed to and counted 12 oranges.

The truth of the statement "I have a dozen oranges here" is established if these four statements are true.

But the four statements are not all of the same kind. They are of two different kinds, and it is important that we examine the proper strategy for establishing the truth of each kind.

Statements like (a) and (b) are known technically as *analytic* statements. They are true by definition.

Statements like (c) and (d) are known technically as *empirical* statements. They are true because they correspond to states-of-affairs, in this case.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #6 on page 10 (continuing on page 12). Become familiar with the differences between *analytic* and *empirical* statements, and especially the way in which the truth of each is established.

COMMENTARY #6, continued

confirmed by a *Correspondence* strategy, since observable instrument readings could be compared to *analytic* statements about pressure in a confined space. However, if the experimenter reported to you, "There are only a very few hydrogen molecules left in this tube," a *Coherence* strategy would have to be used to determine the truth of his report. A *Coherence* strategy depends, not on looking and pointing, but on the coherence of a statement with other statements--in this case, statements about postulated entities from atomic-molecular theory. The consistency of a statement with other statements is the way to consider its truth, according to this truth strategy. As noted on page 9, this is a matter of theoretical coherence, and the way to make sense out of such a statement is on the basis of theoretical considerations. We will be examining the use of a *Coherence* truth strategy in more detail in later sections.

The third way to establish the truth of an *empirical* statement is known technically as the *Pragmatic Theory*. Basically, the "*Pragmatic* strategy" for determining the truth of an *empirical* statement asks, "Is this way of thinking about the events (objects) a useful way?" We will postpone detailed discussion of the "*Pragmatic* strategy" until a later COMMENTARY. It is sufficient at this point to note that it is the third of three possible ways to establish the truth of an *empirical* statement.

Some References

1. A very highly technical, but complete account of the distinctions between *analytic* and *empirical* statements can be found in A. J. Ayer's book Language, Truth and Logic, published by Dover Publications, Inc., in 1952. The account we have given here is based on Professor Ayer's thinking.

2. To see how these distinctions among *analytic* and *empirical* statements can be applied in the analysis of science teaching materials, you might find it interesting to study Brent Kilbourn's booklet Analyzing the Basis for Knowledge Claims in Science Textbooks: A Method and a Case Study, published as "Background Paper No. 6 of The Explanatory Modes Project," by the Department of Curriculum, The Ontario Institute for Studies in Education, 1971 (Toronto).

3. The three "theories of truth" for *empirical* statements--*Correspondence Theory*, *Coherence Theory*, and *Pragmatic Theory*--are briefly outlined in Dictionary of Philosophy, edited by Dagobert D. Runes and published by Littlefield, Adams and Co. of Totowa, New Jersey, in 1968. See p. 321 especially. A most useful elaboration of *Correspondence Theory* and *Coherence Theory* is found in John Hospers' book An Introduction to Philosophical Analysis (second edition), published by Prentice-Hall, Inc., of Englewood Cliffs, New Jersey, in 1967. See p. 115 and p. 116, especially. Finally, *Pragmatic Theory* is presented well in George Kneller's book Introduction to the Philosophy of Education, published by John Wiley and Sons, Inc., in 1964. See p. 48, especially.

Now let us consider how to recognize a mole, using the same approach as we used for the dozen oranges. Suppose someone said to you, "I have a mole of oxygen here." How would the truth of that statement be established?

Let us look again at the same textbook quoted on page 1 and page 5. The passage below[1] follows immediately after the passage quoted on page 5.

> Consequently, chemists based the definition of the mole upon a chosen *weight* rather than a chosen number of particles. During the nineteenth century, chemists decided that the number of molecules in a sample of oxygen weighing exactly 32 grams would be taken as a standard number. Thus defined, *a mole is the number of oxygen molecules in exactly thirty-two grams of oxygen.* The significance of a mole is most usefully connected with this number of particles, rather than the weight. The number, found later to be 6.02×10^{23}, *is called Avogadro's number.*

As we did for the oranges, let us separate the statement "I have a mole of oxygen here" into four parts.

(a) Oxygen *is defined as* a gas with certain chemical and physical properties. (So I can tell the difference between oxygen and non-oxygen--like hydrogen and chlorine--by *definition* of what oxygen is.)

(b) "One mole of oxygen" *is defined as* the amount of oxygen weighing exactly 32 grams.

(c) I identified the gas in my sample as oxygen, consistent with (a).

(d) I pointed to and counted the number of grams of standardized mass necessary to counterbalance my oxygen sample as 32 grams.

So the truth of the statement " I have a mole of oxygen here" is established, as it was in the case of the dozen oranges, if these four statements are true. Statements (a) and (b) are *analytic*, and are therefore true by definition. Statements (c) and (d) are *empirical*, and the truth of each is established by a *Correspondence* strategy.

We can now answer a question posed at the beginning of this booklet: "How can I recognize a mole?" (chemistry-type). A mole of oxygen is recognized by its weight, not by counting some number of particles. What about recognizing a mole of other substances, for example a mole of sugar (let's say it's glucose, $C_6H_{12}O_6$), in our problem on page 7? Same strategy. All we do is start with a different (a) and (b), specifying glucose instead of oxygen. For (b), calculate for $C_6H_{12}O_6$ the "molecular weight" (Pimentel, pp. 33-34), or the "molar mass" (O'Connor, pp. 32-33).[2] We recognize a

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[1] Pimentel, op. cit., p. 33. A similar passage appears in O'Connor et al., op. cit., p. 32.

[2] The terms "molecular weight" and "molar mass" mean the same.

COMMENTARY #7

The statement "32 grams of oxygen contain 6.02 X 10^{23} oxygen molecules" is an *empirical* statement because it is an effort to say something about "the world of objects and events." However, since molecules are postulated entities, it is not the same as a statement like "The 32 classrooms in Learnalot Secondary School contain 1,120 chairs" (also an *empirical* statement). A *Correspondence* truth strategy would work, to determine whether the statement about number of chairs is true. Just point at the chairs and count them.

But a *Correspondence* strategy would not work, to determine whether the statement about number of molecules is true. The indirect evidence referred to in COMMENTARY #4 permits one to make *empirical* statements about atoms, molecules, positive ions, etc., and this evidence is indeed from observations of states-of-affairs. But the postulated entities themselves were not observed, in the collection of that evidence. That is why a *Correspondence* truth strategy will not work, and that is also why the evidence is called "indirect evidence."

A *Coherence* truth strategy is needed to determine whether the statement "32 grams of oxygen contain 6.02 X 10^{23} oxygen molecules" is true. *Coherence* strategies are complicated, and the one required to arrive at Avogadro's number is more complicated than most. Since all we wish to do is demonstrate how a *Coherence* strategy works, let us use the simpler example from COMMENTARY #6, on pages 10 and 12.

Our experimenter is evacuating a glass tube filled originally with pure hydrogen, and reports that the pressure is down to 10^{-5} atmosphere. He then goes on to make another *empirical* statement: "There are only a very few hydrogen molecules left in this tube." Let us separate the statement into several parts, as we did with the statements about the dozen oranges and the mole of oxygen (page 11 and page 13).

(a) Hydrogen *is defined as* a gas having certain chemical and physical properties. (So our experimenter can tell the difference between hydrogen and non-hydrogen--like oxygen and nitrogen--by definition of what hydrogen is.)

This is an *analytic* statement, and therefore is true by definition.

(b) I have pure hydrogen in this tube.

This is an *empirical* statement, and its truth can be determined by a *Correspondence* strategy.

(c) The pressure gauge on this apparatus gives an indication which *is defined as* the pressure of gas remaining in the tube, according to this gauge.

This is an *analytic* statement, and therefore is true by definition.

(d) The pressure gauge indicates that the pressure of the hydrogen is 7.6 X 10^{-3} mm of mercury.

This is an *empirical* statement, and its truth can be determined by a *Correspondence* strategy.

COMMENTARY #7 continues on page 16 . . .

mole of glucose as 180.156 grams of glucose.[1] No counting. The correspondence we seek is between the actual weight of glucose we have [as in (d)], and an analytic statement on the meaning of "a mole of glucose" [as in [b]).

Similarly, our experimenter mentioned on page 1 would know how many moles of copper he deposited, in electroplating, by using a *Correspondence* truth strategy. He would have to know that the *analytic* statement "One mole of copper *is defined as* 63.5 grams of copper" is true, and then he would have to know how many grams of copper had been deposited. If he found that he had deposited exactly 0.635 grams of copper, he would know that the *empirical* statement "0.635 grams of copper were deposited" is true. The correspondence between the weight of copper deposited and the weight of copper defined as "one mole of copper" would tell him, by division, that he deposited 0.01 moles of copper. Notice that he would not count anything.

1.6. Avogadro's Number and *Coherence* Truth Strategy

The truth of such a statement as "I have deposited exactly 0.01 moles of copper" is determined appropriately by a *Correspondence* truth strategy based on a comparison of weights. Then why is the number 6.02×10^{23} (Avogadro's number) mentioned at all in the text passage quoted on page 13? As noted earlier, an "everyday language" interpretation suggests that it is possible (but not practical) to use a "pointing and counting" *Correspondence* strategy to recognize a mole (or part of a mole). It suggests our experimenter has a choice of *Correspondence* strategies (as in the example about sugar, on page 7). We know that is not the case. Let us see why.

The statement "One mole of oxygen is exactly 32 grams of oxygen" is *analytic*. It permits you to check for *empirical* correspondence to states-of-affairs. But "32 grams of oxygen contain 6.02×10^{23} oxygen molecules" is an *empirical* statement. It cannot be checked by a *Correspondence* truth strategy, though. (This is just another way to say that it is not possible to point at and count postulated entities.)

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #7 on page 14 (continuing on page 16). A *Coherence* truth strategy will work, for claims about postulated entities.

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[1]The relative atomic weights used are those found in Pimentel, op. cit., inside back cover. The corresponding list in O'Connor et al., op. cit., is also found on the inside back cover, but is called "molar masses."

COMMENTARY #7, continued

The next statement should be: "The pressure of hydrogen against the working parts of the gauge is caused by the continuous bombardment of hydrogen molecules," which would be an *empirical* statement. However, "hydrogen molecule" is a postulated entity. It cannot be observed, so we are at the end of our rope with *Correspondence* strategy at this point.

It is time to shift to *Coherence* strategy and in order to do this we need to use at least one theoretical statement. We need this so that we can shift from the "observable realm" to the "explanatory realm," as noted in COMMENTARY #3. (In fact, we will use the same kind of example as we used in COMMENTARY #3, and it might be helpful if you reviewed it before continuing here.)

Let us try this, for our theoretical statement.

(e) The behavior of the postulated entities we call "hydrogen molecules" is very much like the behavior of a few ball bearings in a closed box which is being shaken; that is, the molecules constantly bombard the walls of a container in the same way as the ball bearings constantly bombard the walls of the box. (You might wish, at this point, to read again about the "particle explanation of gas pressure" in Pimentel, op. cit., pp. 6-7 and p. 18, or in O'Connor et al., op. cit., p. 9.)

This is an *empirical* statement, but it is about postulated entities and is therefore theoretical. Its truth depends on its coherence--that is, its logical consistency (see page 9)--with all of the rest of atomic-molecular theory, which in turn depends on the validation procedure discussed in COMMENTARY #4. To assert that this single statement is true is to depend on its theoretical coherence with atomic-molecular theory, which is how *Coherence* truth strategy works. (That is where the strategy gets its name.)

That is enough to bridge the gap. We are now in the explanatory realm, and can proceed to the following statement (the one we want to make, as stated above).

(f) The pressure of hydrogen against the working parts of the gauge is caused by the continuous bombardment of hydrogen molecules.

This is an *empirical* statement about the postulated entities "hydrogen molecules." Its truth depends on its theoretical coherence (that is, its logical consistency) with statement (e), above. So its truth can be determined by a *Coherence* strategy.

(g) There are only a very few hydrogen molecules left in this tube.

This is also an *empirical* statement about the postulated entities "hydrogen molecules." Its truth, like that of statement (f) above, depends on its theoretical coherence with other statements: in this case (d), (e), and (f) above. So its truth likewise can be determined by a *Coherence* strategy.

As mentioned earlier, a *Coherence* truth strategy is extremely complicated. Yet it is very commonly used in science. Your understanding of statements in a science text is made much easier if you bear in mind that it is *Coherence* strategy, rather than *Correspondence* strategy, which is most often being used.

It might be useful at this point, to reread Section 2-1 (pp. 18-21) in Pimentel, op. cit., or Sections 1-5 and 1-6 (pp. 7-10) in O'Connor et al., op. cit. Try to identify the places at which a *Coherence* truth strategy is being used, in order to become more familiar with the way it works.

So the truth of the statement "32 grams of oxygen contain 6.02 X 10^{23} oxygen molecules" is established by a *Coherence* strategy, in precisely the same way as our final statement (g) in the example on page 16. In the case of Avogadro's number, of course, there was a calculation of the number of molecules rather than a statement roughly estimating a number ("only a very few hydrogen molecules left"). But the strategy for determining the truth of the statement is the same: coherence with other statements.

As a final note concerning the coherence of a statement about Avogadro's number with other statements, it is revealing to examine science textbooks written at a time when the "accepted value" was not 6.02 X 10^{23}. Theoretical statements about the postulated entities of atomic-molecular theory have changed, as further experimental work has been done. Consequently, statements which are coherent with those statements have to change also. So the "accepted value" of Avogadro's number is coherent (logically consistent) with the most recent "accepted" theoretical statements from which it is calculated.

Let us briefly look at two examples. The first is from a textbook on thermodynamics written by the distinguished British scientist, Sir James Jeans, and published originally in the early 1900's. (The book this example is taken from was published as a fourth edition in 1925.)[1]

Sir James discusses two different calculations of Avogadro's number. The first gives 6.062 X 10^{23}, and is calculated from one set of theoretical statements, used to interpret and explain observations of one kind. The second gives 6.03 X 10^{23}, and is calculated from another set of theoretical statements, used to interpret and explain other observations. Sir James chooses to use the value 6.062 X 10^{23}, apparently placing more confidence in the theoretical statements with which this calculation is coherent.[2] Again, this is how *Coherence* truth strategy works. (See COMMENTARY #7.)

The second example is from a textbook published in 1933,[3] which reports the accepted value of Avogadro's number as 6.064 X 10^{23}. The value is stated as the accepted value because the authors have confidence in the theoretical statements with which the value is logically consistent, or coherent.

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[1]Sir James Jeans, The Dynamical Theory of Gases (4th ed.; New York: Dover Publications, Inc., 1954. The original 4th ed. was published by Cambridge University Press in 1925.)

[2]Ibid., p. 8.

[3]G. P. Harnwell and J. J. Livingood, Experimental Atomic Physics (1st ed.; New York: McGraw-Hill Book Co., 1933), p. 111.

COMMENTARY #8

If the word "mole" were (incorrectly) given an "everyday-language" interpretation, and thought of as a convenient counting word, then its value would have been:

606,200,000,000,000,000,000,000 (in 1925),[1]

606,400,000,000,000,000,000,000 (in 1933),[2] and

602,000,000,000,000,000,000,000 (now).

Imagine the plight of anyone counting the pine needles or sugar granules (page 3 and page 7, respectively), and trying to make some statement about how many it took to make up a mole of those "states-of-affairs objects."

That would be like saying "dozen" meant 7.5 in 1925, and 10 in 1933, and 12 now, or something of the sort. Our problem is that the statement "A mole is 602,000,000,000,000,000,000,000 postulated entities from atomic-molecular theory" is not an *analytic* statement. (On the other hand, the statement "One dozen objects is defined as 12 objects" is an *analytic* statement.) The statement defining the number of postulated entities in a mole is an *empirical* statement, the truth of which is based on *Coherence* truth strategy--not definition. The number 6.02×10^{23} is a theoretical number, not a defined number.

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[1]Sir James Jeans, op. cit., p. 8.

[2]Harnwell and Livingood, op. cit., p. 111.

Because we have seen how *Coherence* truth strategy works, we can understand how the "accepted" value of Avogadro's number can be different in the 1920's (6.062×10^{23}), the 1930's (6.064×10^{23}), and the 1960's (6.02×10^{23}). Although the numbers differ, at each of these three points in time, the basis for accepting each one is the same: it is coherent with a body of the most refined and dependable theoretical statements available at that time. As the theoretical statements change, the number calculated from them has to change also, in order to preserve coherence.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #8 on page 18 (facing this page). Notice the kind of confusion which would arise, if Avogadro's number were (incorrectly) thought of as a "convenient counting word," instead of as a theoretical number.

1.7. Summary: The Significance of Avogadro's Number

Since you can't recognize a mole by the Correspondence truth strategy of pointing and counting, what is the significance of Avogadro's number? Why does the text passage quoted on page 13 say that the significance of a mole is most usefully connected with a number of particles, rather than the standardized weight "32 grams of oxygen"?

Let's review where we've been, for a moment. On page 5 it was pointed out that the word "mole" is properly used only to refer to a theoretical number of postulated entities in atomic-molecular theory. We saw also that trying to recognize a mole of some chemical substance is a states-of-affairs operation, but it has nothing to do with the *Correspondence* truth strategy of pointing and counting. Instead, it requires a *Correspondence* strategy having four parts, such as the strategy shown on page 13 for recognizing a mole of oxygen.

We saw also how to recognize a mole of chemical substances other than oxygen. On pages 13 and 15, the strategy for recognizing a mole of glucose and a mole of copper was based on the use of the relative atomic weight table. In each case, it was necessary to establish an *analytic* statement which *defined* the weight of a mole of each of the two substances. Then an *empirical* statement about the weight of whichever substance we actually have permits us to recognize how many moles of that substance we have. We simply "translate" the number of grams into a number of moles.

COMMENTARY #9

So far, in PART 1 of this booklet, we have been using techniques from analytic philosophy to talk about statements in modern, accepted chemical theory. In PART 2 we will be using the same techniques. We will distinguish between states-of-affairs observations and statements about postulated entities, we will be looking at the kind of "truth strategy" being used, and we will be distinguishing between analytic and synthetic statements. But the statements we will examine were made in the 1800's, and some of them are not accepted today. You might at this time wish to review the COMMENTARIES in PART 1, in order to be sure you feel confident about the distinctions you will need to make.

For example, we will begin PART 2 with an examination of John Dalton's efforts to establish a table of relative atomic weights. The question is this. How could anyone establish the truth of such a statement as "An atom of oxygen is X times as heavy as an atom of hydrogen"? This is the kind of problem Dalton tackled.

Let us begin PART 2, then, and see how he went about it.

Thus, the significance of Avogadro's number has nothing to do with recognizing a mole: the number is not needed, in translating grams into moles. So what <u>is</u> its significance? Let us look at it this way. A mole of oxygen, a mole of glucose, and a mole of copper: each one weighs a different amount (an amount we can calculate from the table of relative atomic weights). Yet the mole concept permits us to say that each mole contains precisely the same number of postulated entities of its own kind. It relates a number of postulated entities to an observable states-of-affairs operation: weighing. It permits us to establish by *Coherence* truth strategy that 6.02×10^{23} oxygen molecules weigh 32 grams, 6.02×10^{23} glucose molecules weigh 180.156 grams, and 6.02×10^{23} copper atoms weigh 63.5 grams. Therefore, by further application of *Coherence* truth strategy (together with some division), we can establish the (theoretical) weight of a <u>single</u> oxygen molecule, or glucose molecule, or copper atom.

The significance of Avogadro's number is twofold, then. *First, it is the <u>same</u> number for all the postulated entities of atomic-molecular theory.* This is the <u>standardizing</u> function of the mole concept. *Second, it permits us to talk systematically about the behavior of postulated entities by using an observable property: weight.* (That is, it relates the "explanatory realm" to the "observable realm," to use the language of COMMENTARY #3.) This is the <u>explanatory</u> function of the mole concept. Its development was a spectacular achievement.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #9 on page 20 (facing this page). We have used the table of relative atomic weights, and have seen how it is used to recognize a mole of any chemical substance. But how does anybody compare the relative weights of <u>atoms</u>? This COMMENTARY lays some groundwork for exploring that question in PART 2 of the booklet.

COMMENTARY #10

By the time Dalton was pursuing his investigations, chemistry was advanced enough that certain chemical elements (as we know them) could be identified accurately. So Dalton had information available to him about the chemical and physical properties of a number of elements, especially gases: hydrogen, nitrogen, and oxygen, for instance. (Dalton worked a great deal with compounds of hydrogen and other elements.) In addition, laboratory techniques had advanced to the point where it was possible to weigh gases.

Imagine an example. Dalton decomposes 30 grams of some gas to get 3 grams of hydrogen and 27 grams of (gaseous) element X: a weight ratio of 1 part hydrogen to 9 parts X. From such an observable weight ratio, Dalton would claim that the postulated entity "one atom of X" is 9 times as heavy as the postulated entity "one atom of hydrogen," provided the original substance was made up of one atom of X for each atom of hydrogen. (We will see later how Dalton made that assumption, and under what conditions.) Hydrogen was chosen as the "baseline" for Dalton's weight ratios because it was the lightest substance known.

This is a familiar problem, then. How do we establish the truth of the statement "One atom of X is 9 times as heavy as one atom of hydrogen"? Let us try starting with the *Correspondence* truth strategy demonstrated on page 11 and page 13 of this booklet. We separate the statement into several parts.

(a) Hydrogen *is defined as* a gas having certain chemical and physical properties. (So Dalton could tell the difference between hydrogen and non-hydrogen--like oxygen and nitrogen--by definition of what hydrogen is.)

This is an *analytic* statement, and therefore is true by definition.

(b) Gaseous element X (whatever it might be) *is defined as* a gas with certain chemical and physical properties. (So Dalton could tell the difference between X and non-X--like Y or Z--by definition of what X is.)

This is also an *analytic* statement, and therefore is true by definition.

(c) One number is 9 times as great as another number *by definition*, if the first number divided by the second gives a result of 9.

This is also an *analytic* statement, and therefore is true by definition.

(d) (In our imaginary example) Dalton identified the first gas as hydrogen, and determined that its weight was 3 grams.

This is an *empirical* statement, and its truth (for our imaginary example) could have been determined by a *Correspondence* strategy.

(e) (Again, in our imaginary example) Dalton identified the other gas as X, and determined that its weight was 27 grams.

This is also an *empirical* statement, and its truth (for our imaginary example) could also have been determined by a *Correspondence* strategy.

COMMENTARY #10 continues on page 24 . . .

PART 2. A BRIEF ACCOUNT OF THREE MAJOR CONTRIBUTIONS TO THE DEVELOPMENT OF THE MOLE CONCEPT

This second part of the booklet examines selected aspects of the thinking of three chemists in the early 1800's: Dalton, Gay-Lussac, and Avogadro. It is not our intention to try to trace the entire development of the mole concept. That is unnecessary and also is much too lengthy a process, for the purposes of this booklet. We will examine some of Dalton's thinking concerning the establishment of a table of relative atomic weights, but again we will not trace the development of the table of relative atomic weights as we know it today. We will examine some of Gay-Lussac's very skilled experimental work on combining volumes of gases, and some of his thinking based on that work. But we need to examine just enough to show why Dalton and Gay-Lussac clashed over their different explanations for the same states-of-affairs information about the decomposition of gases. It was Avogadro who proposed a resolution to their clash, and we will examine some of his thinking to show how the resolution occurred.

Clearly, these three chemists are not the only ones whose work stimulated the development of the mole concept as we know it today. Similarly, these three major contributions to the development of the mole concept do not tell the entire story of how it came to be. They are selected for attention here because they illustrate how these chemists made the "jump" from the "observable realm" of *states-of-affairs* information to the "explanatory realm" of talking about the behavior of *postulated entities*. Thus, it is our intention in this part of the booklet to show how a table of relative atomic weights <u>can</u> be developed, and to show how empirical statements <u>can</u> be made about the number of postulated entities in a volume of gas (for instance).

2.1. John Dalton's Relative Atomic Weights

Like many other scientists in the early 1800's, Dalton experimented with the decomposition of substances by the use of electricity. He then made use of the <u>observable</u> weight ratios of the elements he obtained as a basis for talking about the <u>theoretical</u> weight ratios of his postulated entities "atoms."

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #10 on page 22 (continuing on page 24). Let us examine the kinds of truth strategies Dalton had to be using, with this approach.

COMMENTARY #10, continued

(f) The weight of X Dalton obtained (27 grams) was 9 times as much as the weight of hydrogen obtained (3 grams).

This is also an *empirical* statement, and again its truth (for our imaginary example) could have been determined by a *Correspondence* strategy.

So far, we can use a *Correspondence* truth strategy, for this typical (but imaginary) data of Dalton's, in just the same way as we used that strategy for our examples concerning the oranges and the mole of oxygen, on page 11 and page 13, respectively. But to go the next step, and say something about the postulated entities "atom of X" and "atom of hydrogen," we need to shift now to a *Coherence* strategy. (It might be helpful at this point to review COMMENTARY #7, on pages 14 and 16.)

Recall that, for a *Coherence* truth strategy, some statement is said to be true if it is coherent with other, theoretical statements. Dalton's conclusion, for this imaginary example, would be "One atom of X is 9 times as heavy as one atom of hydrogen."

Let us examine the theoretical statements he used by *Coherence* strategy, in order to "bridge the gap" between statement (f), above, and his conclusion. These theoretical statements are like missing pieces in a jigsaw puzzle at this point. We return to our story now, to see what these statements were. Also, we will look at a "real" example of data known to Dalton.

This account of the thinking of Dalton, Gay-Lussac, and Avogadro is based in part on information found in a booklet edited by Leonard Nash, titled The Atomic-Molecular Theory.[1] Nash has reproduced excerpts from the first published account of Dalton's theory, which appeared in the third edition of a book by Thomas Thomson, published in 1807 and titled A System of Chemistry. Nash estimates that Thomson's account, which was printed with Dalton's permission (and came a year before Dalton's own book), reflects Dalton's thinking in about 1804.[2] It is important to establish this timing, for reasons which will become clear later in our account.

Thomson, citing experimental data known to Dalton, wrote that it had been "proved by analysis" ("analysis" here meaning decomposition by electricity) that 85 2/3% of the weight of water was due to oxygen, and the remaining 14 1/3% of the weight was due to hydrogen.[3] This would mean the ratio of oxygen to hydrogen in water is almost exactly 6:1 by weight.

By modern standards, this is a crude analysis; the modern determination is almost exactly 8 times as much oxygen as hydrogen in water, by weight. Nevertheless, let us consider the observable states-of-affairs information which Thomson reported on Dalton's behalf.

From COMMENTARY #10, we know that Dalton would conclude from this weight ratio that the postulated entity "one atom of oxygen" weighs 6 times as much as the postulated entity "one atom of hydrogen." In addition, he would say that the postulated entity "one 'atom' of water" is 7 times as heavy as the postulated entity "one atom of hydrogen." (Dalton used "atom" in referring to both elements and compounds, but specified that he meant "compound atom" when referring to compounds. We will use his terms also.)

In modern chemical symbols, using "H" for hydrogen and "O" for oxygen, we would write the chemical formula for water as "HO," if we used Dalton's

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[1]Leonard K. Nash, ed., The Atomic-Molecular Theory (Cambridge, Mass.: Harvard University Press, 1950). Nash's booklet is Case 4 in the Harvard Case Histories in Experimental Science, general ed. James B. Conant. (There are 8 such "Cases" altogether, available individually as booklets or in two bound volumes from Harvard University Press.) As OPTIONAL FURTHER READING, this work of Nash's is highly recommended.

[2]Ibid., p. 25. The passage from Thomson's book is on pp. 25-27. Nash cites the Thomson passage as 3rd ed. (1807), vol. 3, p. 425, and gives as a more accessible source the Alembic Club Reprint No. 2, Foundations of the Atomic Theory (E. and S. Livingstone, Teviot Place, Edinburgh, Scotland).

[3]Ibid., p. 26. (Also, Nash notes the weight ratio on p. 24.)

COMMENTARY #11

First, we express algebraically a statement accounting for the weight of the oxygen produced.

n (atoms of oxygen produced) x o (the weight of one oxygen atom) = 12 grams

Next, we do the same for the weight of the hydrogen produced.

n (atoms of hydrogen produced) x h (the weight of one hydrogen atom) = 2 grams

Therefore, since $n \times o = 12$ grams, and $n \times h = 2$ grams, o must be 6 times as great as h.

Given the *two theoretical statements* he used, Dalton could arrive at no other conclusion than the one he did: the postulated entity "one atom of oxygen" is 6 times as heavy as the postulated entity "one atom of hydrogen."

thinking. That is, he was theorizing that the "compound atom" water is made up of one atom of oxygen and one atom of hydrogen, the former weighing 6 times as much as the latter. By simple algebra, let us see how this theoretical weight ratio for the postulated entities would account for Dalton's observable weight ratio of the gases produced. That way we will see the kinds of theoretical statements he had to make.

Suppose Dalton decomposed 14 grams of water, and obtained 12 grams of oxygen and 2 grams of hydrogen. (There we see the observable weight ratio of 6:1.) His *first theoretical statement* is that every "compound atom" of water contains one atom of oxygen and one atom of hydrogen. His *second theoretical statement* is that the water weighs 14 grams because it consists of some very large number (let's call it "*n*") of these "compound atoms," of water, and each one has a tiny weight (let's call it "*w*"). Likewise, the oxygen obtained weighs 12 grams because it consists of a very large number of oxygen atoms (also *n*, the same as the number of "compound atoms" of water), and each one has a very tiny weight (let's call it "*o*"). Likewise again, the hydrogen obtained weighs 2 grams because it consists of a very large number of hydrogen atoms (again, also *n*, the same as the number of "compound atoms" of water), and each one has a very tiny weight (let's call it "*h*").

Since his thinking was based on these two theoretical statements, Dalton had to conclude (by *Coherence* strategy) that one atom of oxygen is 6 times as heavy as one atom of hydrogen.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #11 on page 26 (facing this page). Let us see why this result was inevitable.

That completes the puzzle we looked at in COMMENTARY #10 (pages 22 and 24). It shows what theoretical statements Dalton had to use, in order to get from statement (f), in COMMENTARY #10, to a statement about relative weights of the postulated entities "an atom of oxygen" and "an atom of hydrogen." That is the essence of *Coherence* truth strategy.

COMMENTARY #12

Dalton theorized first about the number of atoms of hydrogen and oxygen in a "compound atom" of water, and then accounted for the observable weight ratio by assigning different relative weights to the two different kinds of atoms. Suppose we try the reverse approach, theorizing first about the relative weights, and then arriving at the number of atoms of hydrogen and oxygen each "compound atom" of water would have to contain, in order to account for the observable weight ratio.

For a *first theoretical statement* we could say that all atoms of all elements are to be thought to have equal weight (let's call it "*a*"). Then, following the same kind of reasoning used in COMMENTARY #11, we would try to find the relative numbers of atoms of hydrogen and oxygen required to account for the observable weight ratio. (Let us use the example from page 27: suppose Dalton decomposed 14 grams of water and obtained 12 grams of oxygen plus 2 grams of hydrogen. Further, let us use "*b*" as the number of oxygen atoms produced, and "*c*" as the number of hydrogen atoms produced.)

First, we express algebraically a statement accounting for the weight of the oxygen produced. (It might be helpful to refer to COMMENTARY #11 at this point.)

b (atoms of oxygen produced) x *a* (weight of any atom, any substance) = 12 grams

Next, we do the same for the weight of the hydrogen produced.

c (atoms of hydrogen produced) x *a* (weight of any atom, any substance) = 2 grams

Therefore, since $b \times a = 12$ grams, and $c \times a = 2$ grams, b must be 6 times as great as c. That is, the number of oxygen atoms in a "compound atom" of water would be thought to be 6 times the number of hydrogen atoms. As a first try for the formula for water, in modern symbols, we would write HO_6. (But notice that the formula could be H_2O_{12}, or H_3O_{18}, etc. All we have established is that there would be 6 times as many oxygen atoms as hydrogen atoms.) Our strategy, in arriving at this formula, is exactly like Dalton's, except that we begin with a different *first theoretical statement*.

Having done many experiments with gases, and having given considerable thought to their properties, Dalton was insistent that atoms of different substances should be thought to have different weights (another of his *theoretical statements*). Suppose we theorize that each oxygen atom weighs twice as much as each hydrogen atom. Using the same reasoning as above, but noting that the weight of an oxygen atom is theorized to be twice that of a hydrogen atom, we find: $b \times 2a = 12$ grams, while $c \times a = 2$ grams. Therefore, b must be 3 times as great as c. The formula for water, in modern symbols, would be HO_3 (or possibly H_2O_6, H_3O_9, etc., for the reason noted above).[1] Again, our strategy is exactly like Dalton's, except that we have started with a different *first theoretical statement*.

What *first theoretical statement* about the relative weights of oxygen and hydrogen would be needed to make the formula for water HO_2 (H_2O_4, H_3O_6, etc.)? How about HO (H_2O_2, H_3O_3, etc.)?

Dalton's choice was HO (and he didn't have to worry about whether it might be H_2O_2 or H_3O_3), although he didn't use the same symbols we use today. To find out how he made the choice, let us return to our story.

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[1] A somewhat different argument, based on these same principles, is presented by Nash, op. cit., p. 24.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #12 on page 28 (facing this page). The first of Dalton's theoretical statements is rather arbitrary. Let us examine it.

2.1.1. Dalton's "Rule of Greatest Simplicity": Quite an Assumption

Dalton chose HO as the formula for water (using different symbols, which need not concern us here). He did so on the basis of his *first theoretical statement*, above, which is part of his *"rule of greatest simplicity."* It is a reasonable assumption, but nevertheless notice that it is an assumption about the behavior of the postulated entities "atoms" and "compound atoms."

This "rule" deals with several different kinds of compounds, and the first part of it would go something like this (in Dalton's terminology). *If only one compound can be formed when two elements react, then one atom of each of the reacting elements is thought to be combined into a two-part, or binary "compound atom."* Remember that we are talking about the compound water in this case, and to the best of Dalton's knowledge water was the only compound that could be formed from hydrogen and oxygen. (Hydrogen peroxide, H_2O_2 in modern symbols, was unknown to Dalton.)

Before we look at the other parts of the *rule of greatest simplicity*, let us take note of the language shift which occurs in the part of the rule stated above. That is, the sentence begins with a states-of-affairs condition ("If only one compound . . . etc."), and finishes with an explanatory statement telling how Dalton wished to think about the behavior of postulated entities (" . . . then one atom of each . . . etc.").

In Thomson's account of Dalton's ideas (noted on page 25), one further example is given which highlights the first part of the *rule of greatest simplicity*. Thomson wrote that, in the same way the analysis (decomposition) of water into hydrogen and oxygen showed approximately a whole-number weight ratio, the decomposition of ammonia gas into "azote" (nitrogen) and hydrogen showed 80% nitrogen and 20% hydrogen by weight, or a weight ratio of 4:1. Since ammonia was the only known compound of nitrogen and hydrogen, the *rule of greatest simplicity* suggested that one atom of nitrogen combines with one atom of hydrogen, to form one "compound atom" of ammonia. In modern symbols, the chemical formula for ammonia would have to be NH, if Dalton's *rule of greatest simplicity* were followed.

COMMENTARY #13

By applying the first part of Dalton's rule of greatest simplicity to the information reported by Thomson, we see the beginning of a table of relative atomic weights. If hydrogen is assigned a value of 1 (being the lightest substance known), then nitrogen ("azote") gets the value 4 and oxygen the value 6, on the basis of the information Thomson had. He reported these three relative atomic weights in 1807.[1]

Dalton is generally regarded as having been a much more careful thinker than experimenter, and perhaps that accounts for the rather crude analysis which gave rise to the 6:1 weight ratio for oxygen to hydrogen in water. The techniques available at the time were not so crude as to give results so wide of the mark, compared to modern values.[2] But Dalton's major contribution was in the explanatory realm, not the observable realm. He produced a revolution in science by suggesting that all the observable percentages of decomposition experiments should be interpreted as ratios of the weight of one substance to another. This is an explanatory "breakthrough," or a new way of thinking about the data which a number of people knew about, and had known about for many years.[3]

When Dalton published the first part of his work A New System of Chemical Philosophy, in 1808, he had revised the relative atomic weight for nitrogen from 4 to 5, and for oxygen from 6 to 7. (Recall from page 25 that Thomson's book was published in 1807, and Nash estimated that it reflected Dalton's thinking three years earlier, in 1804.) Dalton presented relative weights for 20 elements in his New System, and listed a series of combining weight ratios for 17 compounds, 5 of which are binary. However, water and ammonia are the only two binary compounds he included which were known to be the only possible compound formed by the two elements in question. He also listed both carbon monoxide (CO) and carbon dioxide (CO_2), which he called "carbonic oxide" and "carbonic acid," respectively, as well as other examples of binary and "ternary" (three-part) compounds formed from only two elements. The first part of the rule of greatest simplicity says nothing about these. Let us return to our story, in order to see how Dalton extended his rule of greatest simplicity, so that he could explain the observable evidence about two-element compounds which were not binary.

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[1]Nash, op. cit., p. 26.

[2]Chemists and physicists of the early 1800's made extensive use of the "Voltaic pile" (an electrical battery) in their efforts to determine the composition of substances. (For further information, see the paper by M. Daumas and J. Jacques, in R. Taton, ed., Science in the Nineteenth Century [London: Thames and Hudson Ltd., 1965], pp. 268-302.) For instance, Nash reports (p. 52) that the first published results of the decomposition of ammonia appeared in 1785. As we will see later, Gay-Lussac performed extremely accurate decomposition experiments at the time Dalton was formulating his atomic theory.

[3]Dalton notes, for example, that the Dutch chemists Dieman and Troostwyk had decomposed water by electricity in 1789 (A New System of Chemical Philosophy, Part II, p. 273. Reproduced in facsimile by Wm. Dawson & Sons Ltd., London.) The first part of New System has, fortunately, been reprinted in paperback by Citadel Press in New York (1964), and Dalton's 1808 table of relative atomic weights appears on p. 165 of the reprinted edition. Also, the sections of New System which are most appropriate for our purposes, including the table of relative atomic weights, have been reprinted from the 2nd edition of Dalton's work (1842). They appear in H. A. Boorse and L. Motz, eds., The World of the Atom (2 vols.; New York: Basic Books Inc., 1966), pp. 147-156. These particular sections of New System are highly recommended as OPTIONAL FURTHER READING.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #13 on page 30 (facing this page), and notice what these applications of Dalton's *rule of greatest simplicity* do toward establishing a table of relative atomic weights.

Dalton also included in his rule of greatest simplicity a way to deal with some rather puzzling states-of-affairs information. It was known, in Dalton's time, that "carbonic oxide" (carbon monoxide, to us: CO) and "carbonic acid" (carbon dioxide, to us: CO_2) were both compounds of carbon and oxygen, and no other element. When decomposed, however, they gave different percentages: 44% carbon plus 56% oxygen for the former, and 28% carbon plus 72% oxygen for the latter. Notice that one cannot easily compare the relative weights of the postulated entities "one atom of carbon" and "one atom of oxygen" by using the observable weight ratio, then. This case is not as simple as the ones we examined earlier, for water and ammonia. The relative weights of oxygen, compared to carbon, would have to be either 56:44 (1.27:1) or 72:28 (2.57:1), if we used only the first part of the rule of greatest simplicity.

Let us look at the second part of the rule of greatest simplicity, to see how Dalton resolved this problem. It is worthwhile to quote the background he presented, in his own words.[1]

> If there are two bodies, A and B, which are disposed to combine, the following is the order in which the combinations may take place, beginning with the most simple: namely,
>
> 1 atom of A + 1 atom of B = 1 [compound] atom of C, binary.
> 1 atom of A + 2 atoms of B = 1 [compound] atom of D, ternary.
> 2 atoms of A + 1 atom of B = 1 [compound] atom of E, ternary.
> 1 atom of A + 3 atoms of B = 1 [compound] atom of F, quaternary.
> 3 atoms of A + 1 atom of B = 1 [compound] atom of G, quaternary, &c.

Immediately following that background, Dalton presented the first part of the rule of greatest simplicity. Let us review it, in his own words this time. *"When only one combination of two bodies can be obtained, it must be presumed to be a binary one, unless some cause appear to the contrary."*[2]

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[1]This information is found in Nash, op. cit., p. 24, in the reprint of the first part of New System, op. cit., p. 163, and in the reprinted excerpt from New System, 2nd ed., op. cit., p. 152.

[2]Nash, op. cit., p. 25. Also in the reprint of the first part of New System, op. cit., p. 167, and in the reprinted excerpt from New System, 2nd ed., op. cit., p. 153.

COMMENTARY #14

The first two parts of Dalton's rule of greatest simplicity, and the background for them (presented on page 31), are *empirical* statements about postulated entities. Twice before we have examined the kinds of truth strategies appropriate for determining whether or not a statement of this type is true. In both cases, a combination of *Correspondence* strategy and *Coherence* strategy was seen to be appropriate. In this case, however, we will see that a combination of *Coherence* strategy and *Pragmatic* strategy is needed. At this point, you might find it helpful to review the three kinds of truth strategies described in COMMENTARY #6, and also to re-examine the previous two cases we discussed (COMMENTARIES #7 and #10).

In COMMENTARY #6, it is noted that a *Pragmatic* truth strategy asks this question, essentially: "Is this way of explaining events a useful way?" In this context, "useful" means that the explanation accounts for states-of-affairs. It means also that one can make predictions successfully about states-of-affairs events or objects.

The second part of the rule of greatest simplicity, when used with Dalton's atomic weights, successfully accounted for the observable weight ratios in the two oxides of carbon known at the time, as we have seen. Small wonder that Dalton believed in its truth, then, for here was an instance which supported it by *Pragmatic* strategy. An even more striking instance comes with the third part of the rule, which says to *expect one binary and two ternary compounds, if three different compounds can be formed by two elements.* Three oxides of nitrogen were known at the time Dalton was working. The three possibilities suggested by the third part of the rule are NO (binary), N_2O (the first ternary possibility), and NO_2 (the second ternary possibility). Sure enough, the observable weight ratios could be accounted for successfully using Dalton's atomic weights and the third part of the rule.[1] More confirmation! Again, it suggests the rule is true, by *Pragmatic* strategy.

Where does the *Coherence* strategy show up, in this question about the truth of the rule of greatest simplicity? Just this way. There is logical consistency among all the theoretical statements Dalton made. (Recall from page 9 that we defined this consistency as *theoretical coherence*.) The rule itself is a theoretical statement, being about postulated entities, but he used it in a logically consistent way with other theoretical statements, in order to get to the point where he could try to account for states-of-affairs information (such as our example about the three oxides of nitrogen). At that point, *Pragmatic* strategy takes over.

We have talked about the success of the second and third parts of the rule of greatest simplicity. There are seven parts altogether, but we need go no further. You must by now be wondering why we skipped over the first part of the rule, which suggested that the formula for water should be HO and the formula for ammonia should be NH (refer to page 29). Yet, you know that H_2O and NH_3 are the accepted formulas today. So somehow at least the first part of the rule of greatest simplicity must have been shown to be false.[2] We will see how that happened, in due course.

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[1]Dalton's demonstration of this fact appears in Nash, op. cit., p. 66.

[2]The portions of Dalton's rule of greatest simplicity which survived are expressed in what is known as the "Law of Multiple Proportions" (Pimentel, op. cit., pp. 235-236, and O'Connor et al., op. cit., p. 40). This law simply states that when several compounds can be formed from two elements, the ratio of either element from compound to compound will be a simple whole number (e.g., 1, 2, 3, etc.)

The second part of the rule, of interest to us in our dilemma about the relative weights of oxygen and carbon, is this (again, in Dalton's own words). *"When two combinations are observed, they must be presumed to be a binary and a ternary."*[1] Now, given the background information displayed on page 31, and this second part of the rule of greatest simplicity, we go back to our two oxides of carbon. One would have to be CO (binary) and the other would have to be either C_2O or CO_2, according to Dalton's thinking. (Those are the two ternary possibilities.) If we look at the two weight ratios, 1.27:1 and 2.57:1, we see that the ratio of oxygen to carbon in the second is almost precisely twice what it is in the first. (Twice 1.27 would be 2.54.)

This permits us to account for the observable weight ratios of the two compounds, then, by saying that the postulated entities "carbon atom" and "oxygen atom" combine one-to-one in the first case, and one-to-two in the second. Dalton had established the weight of oxygen (relative to hydrogen) as 7 (refer to COMMENTARY #13). It was then a simple matter for him to note that in CO the weight ratio 1.27:1 for oxygen to carbon would give a relative weight for carbon of 7 divided by 1.27. (The postulated entity "one atom of oxygen" has to weigh 1.27 times as much as the postulated entity "one atom of carbon.") He reported the relative weight of carbon as 5, in the first part of his New System in 1808.

It might be helpful at this point to review the way in which relative weights of the postulated entities "atoms" can account for the observable weight ratios obtained in the decomposition of substances; refer back to pages 23, 25, and 27, and COMMENTARIES #10 and #11, if you wish to review this information.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #14 on page 32 (facing this page). Let us examine the truth strategy needed to determine whether or not these parts of Dalton's rule of greatest simplicity are "true."

2.1.2. Some Problems with the Rule of Greatest Simplicity

You will recall from COMMENTARY #12 (page 28) that the rule of greatest simplicity is arbitrary. That is, we tried several alternatives to Dalton's

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[1]Nash, op. cit., p. 25. Also in the reprint of the first part of New System, op. cit., p. 167, and in the reprinted excerpt from New System, 2nd ed., op. cit., p. 153.

COMMENTARY #15

Dalton's statement that Gay-Lussac and von Humboldt's results were consistent with his thinking requires some analysis on our part. First, Dalton had at his disposal the "fact" (i.e., observation of states-of-affairs) that oxygen was about 14 times as dense as hydrogen. That is, for a given volume of oxygen and hydrogen, the former weighed about 14 times as much as the latter.

Let us review the concept of "density," at this point. It is noted on page 28 of Pimentel, op. cit. (In O'Connor et al., op. cit., refer to Exercise 1-5 on page 16.) Density is the weight of a substance per unit volume, and its greatest utility is for comparing the weights of the same volumes of different substances.

So it is possible to speak of the relative densities of difference substances. Trap the same volume of two different gases, for instance, and weigh them. You then have the relative densities of the two gases, and can say that some volume of gas X weighs so-and-so many times as the same volume of gas Y, as Dalton claimed about the relative densities of oxygen to hydrogen, above (14:1 for oxygen to hydrogen).

"Relative densities" are known technically as "specific gravities," and the value given for any one substance is always relative to a standard. Dalton's standard was the density of atmospheric air (taken to be 1.0), and in his Appendix to Part II of New System he gave, in Table I, the specific gravities" of 16 gases (atmospheric air given the value of 1.0).[1] Oxygen has the value 1.10, and hydrogen the value 0.08, the ratio being about 13.8:1, which Dalton "rounded off" to 14:1.[2]

Dalton commented that the Gay-Lussac and von Humboldt finding, that hydrogen:oxygen was 2:1 by volume in the decomposition of water, was consistent with his relative atomic weights of 7:1 for oxygen:hydrogen. How could this be? Dalton had theorized that water was binary: HO. Thus, its decomposition would yield 1 atom of oxygen for every 1 atom of hydrogen. By weight, the former would be 7 times as heavy as the latter. But if the hydrogen occupied twice as much volume as the oxygen, its density would be 1 weight unit per 2 volume units. The oxygen would have a density of 7 weight units per 1 volume unit. Thus, the relative densities ("specific gravities") would stand in the ratio (hydrogen:oxygen) as $\frac{1}{2}$ to $\frac{7}{1}$, or 1:14. So Dalton's theorizing was completely consistent with the states-of-affairs information of Gay-Lussac and von Humboldt.

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[1]This table appears on p. 560 of the facsimile reproduction of New System, op. cit.

[2]The modern values for density of oxygen and hydrogen, at 0°C and 760 mm of mercury, are 1.42904 g/l and 0.08988 g/l, respectively. The relative densities, then, stand in the ratio of 15.9:1, roughly, by modern standards. These values are from C. D. Hodgman et al. (eds.), Handbook of Chemistry and Physics, 39th ed. (Cleveland, Ohio: Chemical Rubber Publishing Co., 1957), p. 1979.

theorizing that hydrogen and oxygen atoms combine one-to-one, and therefore the formula for water should be HO. We tried HO_6, HO_3, and HO_2, and found that we could account for the observable weight ratio just as well as Dalton did, provided we kept our arguments *theoretically coherent*. All that happens is that we end up with a different set of relative weights for oxygen to hydrogen, i.e., 1:1 for HO_6, 2:1 for HO_3, and 3:1 for HO_2. Dalton made them 6:1, on the basis of the formula HO.

This is an interesting example of how important *theoretical coherence* is in science. The establishment of the table of relative weights depends on what was done about that first part of the rule of greatest simplicity. And the rest is a matter of *theoretical coherence*--that is, logical consistency among the statements being made about the postulated entities "atom of hydrogen," "atom of oxygen," "atom of nitrogen," and so forth. But so long as that first part of the rule of greatest simplicity remains arbitrary, the table of relative atomic weights is based on a very shaky foundation.

When Dalton published the second part of New System, in 1810, he made note that the experimenters Gay-Lussac and von Humboldt had recently reported a very highly refined experiment in which they determined that the volume ratio of hydrogen to oxygen was 2:1, wher water was decomposed. He reported also that the density of oxygen was about 14 times that of hydrogen, concluding that this information was consistent with his thinking that water was a binary compound, and that the relative weights of oxygen and hydrogen atoms were 7 and 1.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #15 on page 34 (facing this page). Let us see how this information is consistent with Dalton's thinking.

Despite the calculation we have just seen, based on the relative weights of 7 for oxygen to 1 for hydrogen (consistent with the first part of the rule of greatest simplicity), Dalton seemed to have some reservations about his rule by this time. Shortly after reporting the information noted above, he says it "must be allowed to be possible that water may be a ternary compound."[1] That, of course, would falsify the first part of his rule, and he seemed at this point to be on the verge of doing just that.

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[1]This information is found on pages 275 and 276 of the facsimile reproduction of New System, op. cit.

COMMENTARY #16

The conversion of weight ratios to volume ratios by Gay-Lussac can be shown readily from his use of Sir Humphrey Davy's weight ratios for the oxides of nitrogen, in his "Memoir . . ."[1] Gay-Lussac reports the following, as the states-of-affairs information obtained by Davy. The figures are percentages.

Davy, from the analysis of various compounds of nitrogen with oxygen, has found the following proportions by weight:

	NITROGEN	OXYGEN
Nitrous oxide	63.30	36.70
Nitrous gas	44.05	55.95
Nitric acid	29.50	70.50

(In modern terminology, "nitrous oxide" retains the same name, and its formula is N_2O; "nitrous gas" is now known as nitric oxide, and its formula is NO; "nitric acid" is now known as nitrogen dioxide, and its formula is NO_2.) Gay-Lussac continues as follows:

Reducing these proportions to volumes, we find:

	NITROGEN	OXYGEN
Nitrous oxide	100	49.5
Nitrous gas	100	108.9
Nitric acid	100	204.7

How did Gay-Lussac get from his first table of states-of-affairs information to his second table of volume ratios?

Recall, from our discussion in COMMENTARY #15, that the density of any substance is defined as its weight per unit volume. The density of nitrogen and the density of oxygen were both known to Gay-Lussac, but unfortunately he did not report the values he used in his "Memoir . . ." Undoubtedly those values are different from modern values. We will use modern values[2] to illustrate the calculation, and will go through one example (nitrous oxide) to show how Gay-Lussac proceeded.

The modern value for the density of nitrogen is 1.25055 grams per liter at 0°C and 760 mm of mercury. (Let us use 1.25, for convenience.) We have, by the definition of density:

$$\text{density of nitrogen} = \frac{\text{weight of nitrogen}}{\text{volume of nitrogen}}.$$

Thus, $$\text{volume of nitrogen} = \frac{\text{weight of nitrogen}}{\text{density of nitrogen}}$$, by algebra. Notice that

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[1]Gay-Lussac, op. cit. This information appears on pages 163-164 of the reprinted version in Boorse and Motz, op. cit., and on page 52 of Nash, op. cit.

[2]The density values for nitrogen and oxygen are from Handbook of Chemistry and Physics, op. cit., p. 1979.

COMMENTARY #16 continues on page 38 . . .

We will come back to Dalton, but first let us examine some of the experimental work and thinking of the French chemist Gay-Lussac.

2.2. Joseph Louis Gay-Lussac's Work on Combining Volumes of Gases

The regularity which Dalton saw in observable weight ratios obtained by combining and decomposing substances was an enormous explanatory breakthrough, as noted in COMMENTARY #13. A similar breakthrough was provided when Gay-Lussac reported a regularity in observable volume ratios (for gases only), in 1809.[1] As noted on page 35, Dalton was aware of the simple volume ratio of 2:1 for hydrogen to oxygen in water, at the time he published the second part of New System in 1810. Gay-Lussac and von Humboldt apparently were brilliant experimenters, and their most careful determination of this volume ratio gave the result 1.9989 volumes of hydrogen to 1.0000 volumes of oxygen, under constant temperature and pressure each time the experiment was performed.[2]

Since he was looking for simple volume ratios in states-of-affairs information, Gay-Lussac proceeded to find them, in abundance, from his own work and that of others. That is why we refer to this thinking of Gay-Lussac's as an explanatory breakthrough. As in the case of Dalton, Gay-Lussac put a new interpretation on states-of-affairs information which had long been available in the published scientific literature of the time. In addition to reporting volume ratios which had been observed directly, by himself and others, Gay-Lussac also used known weight ratios of combining gases, which he converted to volume ratios by using the density of the gases involved. (Many gas densities were known to investigators at that time.)

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #16 on page 36 (continuing on page 38). Here we use one of Gay-Lussac's examples, to review the conversion of weight to volume by using gas density.

2.2.1. Dalton's Interpretation of Gay-Lussac's "Memoir . . ."

After demonstrating that approximate simple whole-number volume ratios were evident in a variety of reactions, Gay-Lussac concluded his "Memoir . . ."

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[1] J. L. Gay-Lussac, "Memoir on the Combination of Gaseous Substances with Each Other." Originally, this paper was published in Mémoires de la Société d'Arcueil, vol. 2 (1809). The English translation is found in Alembic Club Reprint No. 4: Foundation of the Molecular Theory (E. and S. Livingstone, Teviot Place, Edinburgh, Scotland). This same translation has been reprinted in Boorse and Motz, The World of the Atom (op. cit.), pp. 160-170.

[2] Nash, op. cit., p. 45.

COMMENTARY #16, continued

Davy's weight ratios could have any weight units on them, so long as they are consistent. That is, for nitrous oxide, we could say that 63.30 grams of nitrogen and 36.70 grams of oxygen can be obtained by decomposing 100 grams of nitrous oxide. So, if we use 63.30 grams as the weight of nitrogen, we have:

$$\text{volume of nitrogen} = \frac{63.30 \text{ grams}}{1.25 \text{ grams per liter}} = 50.64 \text{ liters.}$$

Now for the oxygen. The modern value for its density is 1.42904 grams per liter, also at 0°C and 760 mm of mercury. (Let us use 1.43, for convenience.) If we go through the same algebraic steps as we did for nitrogen, and use Davy's value for oxygen this time, we have:

$$\text{volume of oxygen} = \frac{36.70 \text{ grams}}{1.43 \text{ grams per liter}} = 25.66 \text{ liters.}$$

We see, then, that the volume ratio of nitrogen to oxygen in nitrous oxide is very nearly 2:1. Gay-Lussac, wanting to make the ratio more obvious, used 100 volume units for nitrogen and then calculated by proportion what the volume of oxygen would be. Thus, 100 is to 50.64 as X is to 25.66, and X turns out to be 50.67. (This differs from the 49.5 value listed by Gay-Lussac because we have used modern density values, which are no doubt different from the ones available in the early 1800's, as noted above.)

You might find it interesting to try this same calculation for "nitrous gas" (nitric oxide) and "nitric acid" (nitrogen dioxide), using the modern value for the density of nitrogen and oxygen.

Clearly, the ratios are not exactly whole-number multiples of each other. Yet it is interesting to notice that the volume ratio for nitrous oxide (N_2O) is almost exactly 2 nitrogen to 1 oxygen. That is, the volume ratio matches the formula. Dalton had written the formula for nitrous oxide as N_2O in the first part of his New System (refer to COMMENTARY #14), on the basis of weight ratios, relative atomic weights, and the third part of his rule of greatest simplicity. Similarly, the (almost) 1:1 volume ratio for "nitrous gas" (nitric oxide, or NO) and the (almost) 1:2 volume ratio for "nitric acid" (nitrogen dioxide, or NO_2) match the respective formulas for these compounds, as Dalton had written them. Again, you have probably noticed that the (almost) 2:1 volume ratio for hydrogen to oxygen in water is identical to the formula as we know it today (H_2O).

One would think Dalton would be pleased at what appears to be a confirmation of many of his formulas (even though he missed on water). He most definitely was not. Let us return to our story and see why.

with a paragraph beginning as follows. "I have shown in this Memoir that the compounds of gaseous substances with each other are always formed in very simple ratios, so that representing one of the terms by unity, the other is 1, or 2, or at most 3."[1] Apparently Gay-Lussac is talking about observable states-of-affairs here--that is, he is only talking about the observed volume ratios. Yet, he says near the beginning of the paper, "Dalton has advanced the idea that compounds of two bodies are formed in such a way that one atom of the one unites with one, two, three, or more atoms of the other."[2] So it is possible to interpret his conclusion as a theoretical statement about the postulated entities "atom of oxygen," or hydrogen, or any other gas, as well as the postulated entities "compound atoms" (Dalton's term).

Whether or not Gay-Lussac intended to make a statement about postulated entities, Dalton interpreted it that way (as we shall see below). The second sentence of the conclusion to the "Memoir . . ." might well have infuriated Dalton. "These ratios by volume are not observed with solid or liquid substances, *nor when we consider weights*, and they form a new proof that *it is only in the gaseous state that substances . . . obey regular laws.*"[3]

Recall that Dalton had painstakingly shown that "substances obey regular laws," whether solid, liquid, or gas, and he had done so by using weight ratios and his table of relative atomic weights. (Dalton's experiments were not confined to gases, by any means, even though the examples we cited earlier were all gases.) All of this work he had published a year before Gay-Lussac's "Memoir . . ." appeared, and Gay-Lussac was obviously aware of his work (or else he would not have mentioned it at the beginning of his paper). The implication of Gay-Lussac's statement, whether he intended it or not, was that all the "regular laws" Dalton had accounted for, through weight ratios and his table of atomic weights, just didn't exist. Do not be surprised, then, to find in the next section that Dalton attempted to discredit Gay-Lussac's work.

Whatever his personal feelings about this apparent insult to all his thinking (and we may be sure they were strong, judging by the way his attack is worded), it was a theoretical point which apparently bothered Dalton more

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[1]Gay-Lussac, op. cit. The conclusion appears on page 170 of the reprinted version in Boorse and Motz, op. cit., and on page 57 of Nash, op. cit.

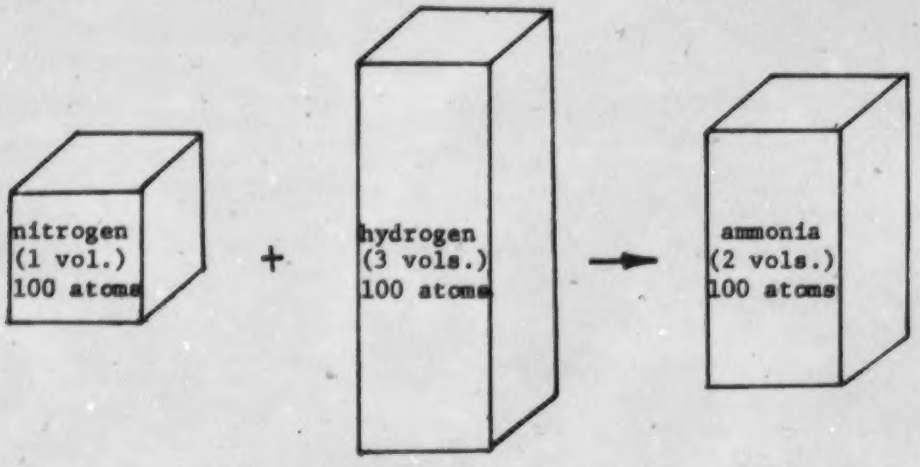
[2]Gay-Lussac, op. cit. This information appears on page 161 of the reprinted version in Boorse and Motz., op. cit., and on page 48 of Nash, op. cit.

[3]Gay-Lussac, op. cit. This information appears on page 170 of the reprinted version in Boorse and Motz, op. cit., and on page 57 of Nash, op. cit. [Italics added.]

COMMENTARY #17

On page 29, we saw that Dalton proposed the formula NH for ammonia, on the basis of weight ratios and the first part of his rule of greatest simplicity. Thus, he was theorizing that 1 atom of nitrogen combined with 1 atom of hydrogen, to produce 1 "compound atom" of ammonia.

According to this reasoning, (for instance) 100 atoms of nitrogen would be thought to combine with 100 atoms of hydrogen to produce 100 "compound atoms" of ammonia. Gay-Lussac observed that 1 volume of nitrogen combined with 3 volumes of hydrogen, to produce 2 volumes of ammonia. Let us consider a diagram representing this information.



Thus, the 100 atoms of nitrogen would be packed into a space 1/3 the volume occupied by the 100 atoms of hydrogen. Also, the 100 "compound atoms" of ammonia would be packed into a space 2/3 the volume occupied by the 100 atoms of hydrogen.

Here is the nature of the reasoning behind the part of the theoretical statement on page 41, which Dalton realized through his interpretation of Gay-Lussac's work (". . . *one gas would contain some simply related multiple of the number of atoms in the same volume of another gas*"). For this example, let us use 6 volumes as our basis for comparison. 6 volumes of nitrogen would be thought to contain 600 nitrogen atoms (refer to the diagram), while 6 volumes of hydrogen would be thought to contain 200 hydrogen atoms, and 6 volumes of ammonia would be thought to contain 300 "compound atoms" of ammonia. Therefore, the number of nitrogen atoms in a given volume of nitrogen gas would be 3 times the number of hydrogen atoms in an identical volume of hydrogen gas, or 2 times the number of ammonia "compound atoms" in an identical volume of ammonia gas. Similarly, equal volumes of ammonia and hydrogen would contain atoms of their respective kinds in the simply related ratio 3 (ammonia) to 2 (hydrogen).

than anything. He interpreted Gay-Lussac's work in the explanatory realm, as suggesting that the observable volume ratios could be directly interpreted as atom-to-atom combinations. (Recall, from COMMENTARIES #10 and #11, and pages 25, 27, and 29, that this is exactly how Dalton moved from the observable realm to the explanatory realm for his own weight ratios, with the assistance of his rule of greatest simplicity and his table of relative atomic weights. So he would quite naturally think about Gay-Lussac's volume ratios in the same way.) On the basis of this interpretation (atom-to-atom combinations identical to volume-to-volume combinations), Dalton realized that the following theoretical statement would have to be true, even though Gay-Lussac had not mentioned it in his "Memoir . . .": *Equal volumes of different gases would have to be thought to contain the same number of atoms (or one gas would contain some simply related multiple of the number of atoms in the same volume of another gas).*

Let us see how Dalton would have arrived at this statement, using the case of nitrous oxide (N_2O) as an example. On the basis of weight ratios, relative atomic weights, and the third part of his rule of greatest simplicity, Dalton theorized that 2 atoms of nitrogen combined with 1 atom of oxygen, to form the "compound atom" N_2O. Therefore, (for instance) 200 atoms of nitrogen would be thought to combine with 100 atoms of oxygen. If the 200 atoms of nitrogen occupied exactly twice the volume of the 100 atoms of oxygen (as Gay-Lussac's ratio suggested), that would mean 100 atoms of nitrogen and 100 atoms of oxygen must occupy the same volume. And so it would be in every case where Gay-Lussac's observed combining volume ratios were identical to Dalton's theoretical formulas.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #17 on page 40 (facing this page), for an example of a case (ammonia) where Gay-Lussac's observed combining volume ratios are not identical to Dalton's theoretical formula.

2.2.2. Dalton Attempts to Discredit Gay-Lussac's Thinking

Gay-Lussac apparently had not intended to be quite so insulting to Dalton as the second sentence of his conclusion to the "Memoir . . ." suggests (noted earlier), for at one spot he refers to "Dalton's ingenious idea that combinations are formed from atom to atom."[1] Nevertheless, Dalton completely

[1]Gay-Lussac, op. cit. This reference to Dalton appears on page 169 of the reprinted version in Boorse and Motz, op. cit., and on page 56 of Nash, op. cit.

COMMENTARY #18

Dalton had some grounds for questioning Gay-Lussac's data. He cited published experimental results which disagreed with those used by Gay-Lussac. For some reactions he could show that even more "rounding off" was required than Gay-Lussac had to do with the examples he used. Apparently, Gay-Lussac considered the necessary approximations he used to be within the bounds of experimental error. But Dalton rejected the whole idea of simple combining ratios for volumes, and so the "rounding off" process was not acceptable to him.

It was Dalton's theorizing which was really at stake, though. If Gay-Lussac's state-of-affairs information were accepted as correct, but could not be accounted for by Dalton's theory, then the theory would have to be changed: *Pragmatic* truth strategy would demand it. (You may wish to refer back to COMMENTARY #14 at this point, to review the workings of *Pragmatic* truth strategy.) One sure way to avoid having to change the theory is to be suspicious of observations which it will not account for, and discount them as being inaccurate or deficient in some way. We may surmise that this is the reason it was important for Dalton to cast doubt on the accuracy of Gay-Lussac's work.

But in what way could Dalton's theory not account for Gay-Lussac's states-of-affairs information? We have asserted that it could not, but have not yet shown why. To do so, we will perform some calculations based on the information about ammonia in COMMENTARY #17. (There is no evidence that Dalton himself performed these calculations for ammonia, but we have noted similar thinking by him about water in COMMENTARY #15. Also, there is no doubt that his theory permitted these calculations to be made at that time.)

Gas densities were of great interest to Dalton. He had come to his studies of the relative weights of atoms through a life-long interest in meteorology, and especially in determining the composition of the earth's atmosphere. Thus he had available states-of-affairs information about the relative densities of a number of gases, as noted in COMMENTARY #15. In addition, Dalton's theory would have permitted him to predict relative densities, based on his theoretical interpretation of Gay Lussac's work. If the prediction (based on Gay-Lussac's work) does not match the observable states-of-affairs information about relative densities (assumed to be accurate), then something in the chain of theoretical statements behind the prediction must be wrong. That is how *Pragmatic* truth strategy works. Let us see what happens, comparing relative densities of ammonia and hydrogen.

From COMMENTARY #17, recall that Dalton's interpretation of Gay-Lussac's information on the combining volumes of nitrogen and hydrogen in the formation of ammonia required that, at the same temperature and pressure, 300 "compound atoms" of ammonia would be thought to occupy the same volume as 200 atoms of hydrogen. Dalton had the (theoretical) relative weights of nitrogen to hydrogen fixed at 5:1 as early as 1808, in his New System. Given his theorizing that ammonia is NH, one "compound atom" of ammonia should weigh 6 times as much as one atom of hydrogen. Therefore, for the same volume, the weight of ammonia present should be 300 times 6 weight units, while the weight of hydrogen present should be 200 times 1 weight unit. The ratio of relative densities of the two gases should be, according to this theorizing, 1800 to 200, or 9 to 1. So this is the prediction,

 COMMENTARY #18 continues on page 44 . . .

rejected the validity of Gay-Lussac's work a year after it was published, in the Appendix to the second part of New System (1810), with the following statement. "The truth is, I believe, that gases do not unite in equal or exact measures [i.e., volumes] in any one instance; when they appear to do so, it is owing to the inaccuracy of our experiments."[1]

Dalton's statement of rejection was the conclusion of about three pages of very blunt criticism.[2] We will now consider some aspects of the basis for his generally negative position toward Gay-Lussac's entire proposal about combining volume ratios. (However, it is not possible to match the superb analysis offered by Nash,[3] and you should refer to his work if you wish to get a more complete picture of Dalton's thinking on this issue.) Dalton's criticism of Gay-Lussac's work has several parts. Rather than examine each in turn, we consider some but look also at ways in which Dalton's theory could not accommodate Gay-Lussac's conclusions. Four points are considered.

First, and of least importance to us in this booklet, is that Dalton seriously questioned the accuracy of Gay-Lussac's experiments, and also the way in which he had "rounded off" numbers to get simple volume ratios. This was very risky for Dalton, since he was known to have "rounded off" his own weight ratios, and his experimental results tended to be crude (while Gay-Lussac was renowned for his experimental technique). Dalton must have had a lot at stake, to take this risky approach.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #18 on page 42 (continuing on page 44), where we consider the reason it was so important for Dalton to cast doubt on the accuracy of Gay-Lussac's observable data.

The second point we consider is the way Dalton theorized about the nature of a gas. He thought of a volume of gas as being completely full of "globular particles" each surrounded by an "elastic atmosphere." Each solid

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[1]Dalton, op. cit., This statement is from page 559 of the facsimile edition of New System, op. cit., and appears on page 68 of Nash, op. cit.

[2]Dalton, New System. In the facsimile reproduction (op. cit.), this information appears on pages 555-559.

[3]If you are interested in reading the entire account of Dalton's position, please see Nash, op. cit., pages 58-69. It is Section 4, titled "The Apparent Inconsistency of the Atomic Theory and the Law of Combining Volumes."

COMMENTARY #18, continued

according to Dalton's theory and our example of the possible theoretical argument he could have made, based on his interpretation of Gay-Lussac's work.

Dalton had determined the actual relative densities for ammonia and hydrogen as 0.60 (ammonia) and 0.08 (hydrogen)[1], a ratio of 7.5 to 1. Clearly, this is different from the predicted ratio of 9 to 1. Something must be wrong in the chain of theoretical statements leading to the prediction (assuming the actual values are accurate). We are suggesting here that Dalton, like most theorists, would have been more likely to cast doubt on another experimenter's findings, than to seriously question his own theory. (You might wish to try this same calculation for nitrogen and hydrogen; Dalton's figure for the relative density of nitrogen was 0.97. The predicted ratio is 15:1 for nitrogen to hydrogen, and the actual ratio of the two relative densities is about 12:1. If you make the comparison for ammonia and nitrogen, you might be surprised.)

Thus we have shown that Dalton's theory at the time could not account for Gay-Lussac's findings. We have also shown, by an argument Dalton could have made (although there is no evidence that he did make it), that *Pragmatic* truth strategy suggests an alteration was needed in the theory. Dalton preferred instead to cast doubt on the accuracy and validity of Gay-Lussac's findings. It was indeed a risky course of action--risky for Dalton's reputation as a scientist.

But three other aspects of Dalton's thinking contributed to his rejection of Gay-Lussac's work. Let us return to our exploration of these.

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[1]This information is reported in Table 1 of the Appendix to Part II of New System, p. 560 of the facsimile reproduction (op. cit.).

"globular particle" was thought to be at the center of a definite space, since rays of the "elastic atmosphere" emanated from the solid particle out to the edges of the definite space. (The term "definite space" is being used here because it appears that Dalton thought of these spaces as spheres in Part I of New System, but he attached to the Appendix to Part II a set of diagrams which make them appear to be cubes.[1] In any event, his was not the conception of a gas we hold today--that is, tiny particles separated by enormous distances, compared to the size of the particles.) Dalton also theorized that atoms and "compound atoms" of different gases had different diameters, which meant in turn that the definite space occupied by each atom of one kind of gas would be different from that occupied by each atom of another kind. Hence a given number of particles of the one gas would have to occupy a volume different from the same number of particles of any other gas. Finally, then, a fixed volume of one kind of gas just could not contain the same number of particles as the same volume of another kind of gas, according to Dalton's theorizing.

Dalton summarized this aspect of his disagreement with Gay-Lussac in the following way. "In fact, his [i.e., Gay-Lussac's] notion of measures [i.e., volumes] is analogous to mine of atoms; and if it could be proved that all elastic fluids [i.e., gases] have the same number of atoms in the same volume, or numbers that are as 1, 2, 3, &c. the two hypotheses would be the same, except that mine is universal, and his applies only to elastic fluids. Gay-Lussac could not but see (page 188, Part I of this work) that a similar hypothesis had been entertained by me, and abandoned as untenable . . . ."[2]

So here we see Dalton rejecting not only the notion that equal volumes of different gases could contain equal numbers of particles, but also numbers which stood in simple, whole-number relationship to each other (1:1, 1:2, 1:3, etc.). This he did on the basis of *Coherence* truth strategy.

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[1]Dalton, New System. In the facsimile edition (op. cit.), these diagrams constitute Plate 8 following page 560, the final page of the Appendix to Part II.

[2]Ibid. This passage is from page 556 of the facsimile edition, and appears on page 63 of Nash, op. cit. Dalton's reference to "page 188, Part I of this work" alludes to the conclusion of an argument based on his way of thinking about the nature of a gas.

COMMENTARY #19

In the example Dalton used, concerning "nitrous gas" (nitric oxide), he is referring to a particular kind of gaseous reaction, and several examples were known at the time. In such reactions, the (observable) number of volumes of the product exceeds the number of volumes of at least one of the reactants. Hence, in the observable realm, we can talk about what happens as follows:

1 volume of nitrogen + 1 volume of oxygen → 2 volumes of nitric oxide
2 volumes of hydrogen + 1 volume of oxygen → 2 volumes of water vapor
1 volume of nitrogen + 3 volumes of hydrogen → 2 volumes of ammonia

In order to see the force of Dalton's point, we need to shift now to the explanatory realm. The argument would go approximately as follows, using the example of nitric oxide.

(a) One atom of nitrogen combines with one atom of oxygen to form one "compound atom" of "nitrous gas" (NO). (This theoretical statement is based on Dalton's Rule of Greatest Simplicity.)

(b) Accordingly, 100 atoms of nitrogen (say) would combine with 100 atoms of oxygen to form 100 "compound atoms" of NO.

(c) But the observable volume occupied by the 100 "compound atoms" of NO would be (according to Dalton) nearly twice as much as the observable volume occupied by the 100 atoms of nitrogen, or the 100 atoms of oxygen. (Gay-Lussac would say it is exactly twice as much.)

(d) Therefore, a given volume of NO does not contain the same number of (theoretical) particles as the same volume of nitrogen or oxygen.

On the basis of his knowledge of this and similar gaseous reactions, and the kind of theorizing shown here (based on his atomic theory as it was then formulated), Dalton generalized that no two gases (probably) would have the same number of particles in identical volumes.

You might find it interesting to go through the argument for the other two examples given above, bearing in mind that Dalton had theorized that the formula for water was HO, and for ammonia NH.

Notice that Dalton is not explicitly rejecting the notion that the number of theoretical particles in a volume of nitrogen (or oxygen) could be twice as many as in the same volume of nitric oxide. But his wording of the statement quoted, to the effect that the volume of "nitrous gas" would be nearly (not exactly) twice as much as the volume of either reactant, confirms what we have already seen: that he did not attach the same significance to volume ratios that Gay-Lussac did.

His theoretical model of a gas, based on considerable thought and experimentation, convinced him that equal volumes of different gases would contain widely varying numbers of particles, and that the numbers would have virtually no relationship to one another.

The two points we have considered so far are taken directly from Dalton's criticism of Gay-Lussac in the Appendix to Part II of New System. The third point, while not mentioned specifically in that criticism, is nevertheless part of the argument to which Dalton refers in the quote above (his reference to "page 188, Part I of this work"). It is an explicit denial of the (theoretical) possibility that equal volumes of gases could contain equal numbers of particles, and it was published in 1808: ". . . if equal measures [i.e., volumes] of azotic [i.e, nitrogen] and oxygenous gas were mixed, and could be instantly united chemically, they would form nearly two measures of nitrous gas [i.e, nitric oxide]. . . but the number of ultimate particles could at most be one half that before the union. No two elastic fluids [i.e, gases], probably, therefore, have the same number of particles, either in the same volume or the same weight."[1] Notice in this quote and in the one directly preceding it (on page 45) that Dalton's language shifts back and forth between the observable realm, when he speaks of volumes, and the explanatory realm, when he speaks of particles, atoms, etc. For this reason, it is a bit difficult to follow Dalton's reasoning, and to see clearly in what manner Dalton and Gay-Lussac are opposed on this point. (Recall that Gay-Lussac had not claimed anything about equal volumes of gases containing equal numbers of particles; that was Dalton's interpretation of the meaning of Gay-Lussac's work, as noted on page 41.)

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #19 on page 46 (facing this page), where we analyze Dalton's statements to see how and to what extent he is disagreeing with Gay-Lussac on this point.

The fourth and final point we consider, like the third, was not mentioned specifically in Dalton's criticism of Gay-Lussac's work. Yet there

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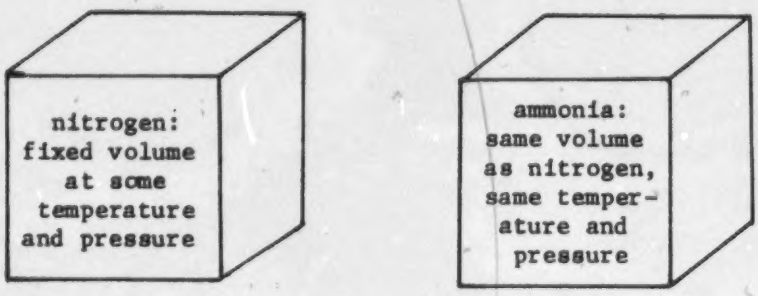
[1] Ibid. This passage is from page 71 of the facsimile edition; it appears on page 59 of Nash, op. cit., and on page 57 of the Citadel Press reprint of Part I of New System, op. cit.

COMMENTARY #20

As noted in COMMENTARY #15, Dalton included a table of specific gravities ("relative densities," compared to a standard of "atmospheric air" as 1.0) in the Appendix to Part II of his New System. Here he listed the specific gravity of nitrogen as .97, and of ammonia as .60. (Modern values also show the density of nitrogen as being greater than that of ammonia.) These figures present us with a strange problem, as they did Dalton: ammonia is nitrogen with hydrogen added to it, and it should therefore be heavier than hydrogen.

This much information is from the observable realm. Let us now shift to the explanatory realm for a moment, to see how to resolve this problem according to Dalton's thinking. Dalton had theorized, on the basis of his Rule of Greatest Simplicity, that 1 atom of nitrogen combined with 1 atom of hydrogen to form 1 "compound atom" of ammonia. Thus a "compound atom" of NH should be heavier than an atom of N.

Since NH is less dense than N (that is, a given volume of NH weighs less than the same volume of N), Dalton had only to theorize that, in the measurement of relative densities, fewer particles of NH were present in a given volume than would be present in the same volume of N. (Indeed, this is consistent with Dalton's theoretical model of a gas, as described on pages 43-47.) We can represent this bit of theorizing with a diagram, as follows.


nitrogen: fixed volume at some temperature and pressure
ammonia: same volume as nitrogen, same temperature and pressure

Dalton observes:	specific gravity .97	specific gravity .60
Dalton theorizes:	full of atoms of N, as suggested by his theoretical model of a gas.	full of "compound atoms" of NH, each one heavier but much larger than each atom of N
Dalton concludes:	contains some number of N atoms	contains a much smaller number of NH "compound atoms" (because each one is so much larger than an N atom)

But wait a minute. Dalton's theoretical interpretation of the meaning of Gay-Lussac's work was that equal volumes of gases would have to be thought to contain equal (or simply related) numbers of particles. This is, clearly, in direct conflict with our resolution of the problem based on Dalton's thinking, unless the "much smaller number" of ammonia atoms referred to above turned out to be some simple fraction (e.g., $\frac{1}{2}$ or $\frac{1}{3}$, etc.) of the number of nitrogen atoms. Let us see.

COMMENTARY #20 continues on page 50 . . .

is evidence that Dalton had been concerned about it for some time, and the point is important for our purposes in this booklet. In certain reactions, gaseous compounds formed from elements are less dense than the gaseous elements from which they are formed. For instance, the density of water vapor (oxygen with hydrogen added to it) is observed to be less than the density of oxygen by itself.[1] Again, the density of ammonia (nitrogen with hydrogen added to it) is observed to be less than the density of nitrogen by itself. Dalton had a way to resolve this problem. But it would have required that he theorize in a way which Gay-Lussac's notion about equal volume ratios, if accepted, would challenge directly.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #20 on page 48 (continuing on page 50), to see how Dalton resolved this peculiar problem, and also how Gay-Lussac's idea of equal volume ratios could not fit with Dalton's solution. We will use ammonia as our example.

2.3. The Impact of Two Suggestions by Amedeo Avogadro

As we have seen, Dalton's theorizing could not accommodate his interpretation of Gay-Lussac's results, when he considered the possibility that equal volumes of all gases contained equal numbers of particles. Four points need to be resolved.

(1) Was Gay-Lussac rounding off his data too much, as Dalton insisted, and therefore "finding" relationships which were artificial, and had no connection to states-of-affairs events occurring in the gases with which he experimented? More accurate experimentation and *Correspondence* truth strategy could be used to answer this question--it is a problem in the observable realm.

(2) Was Dalton's theoretical model of a gas, imagined to be packed full of particles each surrounded by an "elastic atmosphere" and occupying a definite space, an adequate model? This question cannot be answered by more accurate experimentation alone, and therefore cannot be settled by *Correspon-*

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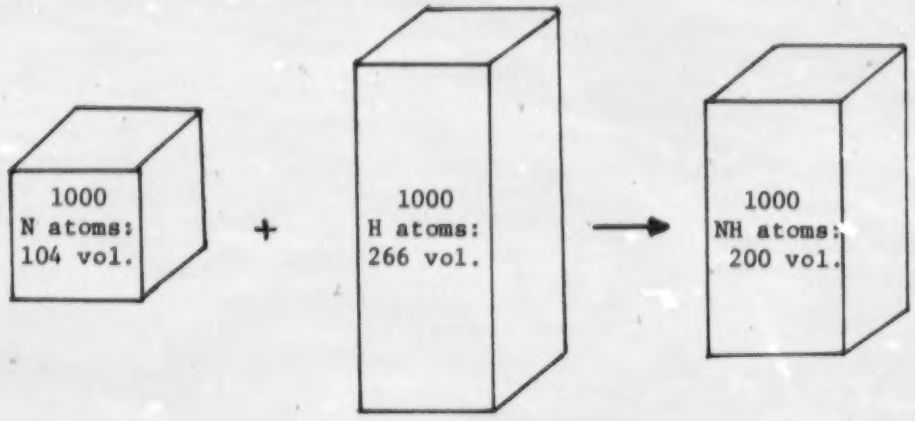
[1]Dalton wrote about this problem in his notebook as early as 1803, according to Nash (op. cit., p. 58): ". . . the ultimate particles of water or steam are certainly of greater specific gravity than those of oxygen, yet the last gas is heavier than steam." Nash cites as a more accessible source A New View of the Origin of Dalton's Atomic Theory, by H. E. Roscoe and A. Harden (London: Macmillan and Co., 1896), p. 57.

Dalton's thinking lets us resolve this problem in a theoretically consistent way, even though it seems complex. His own volume ratios for the production of ammonia (leaving aside Gay-Lussac's ratios for the moment) are reported in the Appendix to Part II of New System: 52 "measures" (i.e., volumes) of nitrogen combine with 133 measures of hydrogen to form 100 measures of ammonia.[1] If we double those, we find 104 volumes of nitrogen combining with 266 volumes of hydrogen to form 200 volumes of ammonia.) Further, Dalton theorized that 1 atom of nitrogen was combining with 1 atom of hydrogen, in this reaction, to produce 1 "compound atom" of ammonia.

Let us represent this information and theorizing in a diagram, assuming for convenience that the 104 volumes of nitrogen contain exactly 1000 atoms.



In order to compare the specific gravities of NH and N, we need to examine the same number of volumes. 104 volumes of N contain 1000 N atoms; 104 volumes of NH would contain a few more than 500.

Does the same line of reasoning hold for the hydrogen in this reaction? (Dalton's figure for the specific gravity of hydrogen was .08.)

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[1] In the facsimile edition of New System (op. cit.), this information is reported in Table 2 on page 560.

dence truth strategy. It involves a complex and interrelated way of thinking about the nature of a gas. Already in Dalton's time other chemists were thinking about the nature of a gas in much the same way as we do today--imagining the tiny (theoretical) particles to be separated by enormous distances, compared to the size of the particles themselves. The model which "wins" in science must be theoretically consistent, by *Coherence* truth strategy, but it must also account for more states-of-affairs information, by *Pragmatic* truth strategy, than the "loser" can.

(3) Is there an alternative way to explain the problem Dalton exemplified with his statement about nitric oxide (page 47 and COMMENTARY #19)? That is, Dalton used a statement from the explanatory realm, to the effect that no two gases have equal numbers of particles in equal volumes, to account for the larger volume of product than reactant in certain gaseous reactions. Can another statement, or set of statements, be used to account for this information with equal success? If a statement (or statements) can be found, then by *Pragmatic* truth strategy it (or they) could be as acceptable as Dalton's explanation, and *Coherence* truth strategy might show it (or them) to be better.

(4) By using Dalton's thinking, our way of resolving the problem of lesser density for heavier gases, in certain reactions, could not accommodate the "equal-volumes-equal-numbers" idea, as we saw in COMMENTARY #20. As in #3 above, we ask if there is an alternative way, and perhaps a better way, to account for this states-of-affairs information.

In 1811 an Italian physicist, Amedeo Avogadro, published a paper in which he elaborated a position concerning all four of these points.[1] By doing so, he demonstrated how Dalton's atomic theory could be used to account for the states-of-affairs information reported by Gay-Lussac.

Avogadro began his paper by accepting Gay-Lussac's simple volume ratios as "brute fact," i.e., as accurate representations of states-of-affairs information. He followed that acceptance with a position statement regarding his theoretical interpretation of the significance of Gay-Lussac's work.

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[1]A. Avogadro, "A Manner of Determining the Relative Masses of the Elementary Molecules of Bodies and the Proportions in Which They Enter into These Compounds." Originally, this paper was published in Journal de Physique, vol. 73, no. 58 (1811). An English translation is found in Alembic Club Reprint No. 4, op. cit. This same translation has been reprinted in Boorse and Motz, The World of the Atom (op. cit.), pp. 175-180.

COMMENTARY #21

Nash points out that Avogadro was not the first person to have advanced the theoretical statement that equal volumes of all gases should be thought to contain equal numbers of particles. Bernoulli had suggested it some fifty years earlier, and Dalton had, as we have seen, recognized that it was a theoretical implication of Gay-Lussac's work.[1]

However, given the clash between Dalton and Gay-Lussac, there were good reasons for accepting the idea as proposed at that particular time in history. (It was not accepted for another fifty years, but for our purposes it resolves several problems and shows the basis on which certain aspects of current atomic-molecular theory emerged from the chaos of the controversy between Dalton and Gay-Lussac.)

Recall that Dalton had theorized, on the basis of his Rule of Greatest Simplicity, that 1 atom of hydrogen combined with 1 atom of oxygen to form one "compound atom" of water: HO. Yet he knew that the volume of hydrogen consumed was roughly twice that of the oxygen (and Gay-Lussac was convinced it was exactly twice as much). If we use Avogadro's notion that equal volumes of different gases contain equal numbers of particles, we would have to change the formula for water from HO to H_2O, to reflect the fact that two hydrogen particles are being used for each oxygen particle, in the reaction. (2 volumes of water are formed also, which leaves us with another problem. Avogadro's second hypothesis resolves that one.)

Similarly, from Gay-Lussac's results, one volume of nitrogen combines with three volumes of hydrogen, suggesting the formula for ammonia should be NH_3, rather than NH (as Dalton had theorized).

[1]Nash, op. cit., p. 73.

"The first hypothesis to present itself in this connection [i.e., in interpreting Gay-Lussac's simple volume ratios], and apparently even the only admissible one, is the supposition that the number of integral molecules in [all] gases is always the same for equal volumes, or always proportional to the volumes."[1]

Three points must be kept in mind, concerning this statement. First, Avogadro is speaking here of gaseous reactions. Second, his use of the phrase "integral molecules" might be somewhat confusing. Think of "particle," when he uses the word "molecule." (Avogadro was not using the term in the sense we use it today.) Third, Avogadro is not necessarily saying, in this first hypothesis, that equal volumes of gases contain equal numbers of particles. He has left the alternative open that the number of particles is proportional to the volumes. Yet, he then goes on to emphasize the former, in his discussion of the nature of a gas, so that we may take it that he is strongly in favor of the theoretical statement that equal volumes of all gases should be imagined to contain equal numbers of particles.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #21 on page 52 (facing this page). Let us see what this theoretical statement does to some of Dalton's formulas for gaseous compounds.

Of the four points to be resolved, in our presentation of the controversy between Dalton and Gay-Lussac, we see already that Avogadro has taken a consistent position on the first two. He has accepted Gay-Lussac's simple volume ratios, which Dalton would not accept. Further, he has necessarily rejected Dalton's theoretical model of a gas, in favor of the model which imagines a gas to be composed of (theoretical) particles separated by very large distances, compared to the size of the particles themselves. (He had to reject Dalton's model, in order to propose the idea that equal volumes of all gases contain equal numbers of particles. Avogadro's discussion of the nature of a gas confirms this.)

Now to the third point: there are some gaseous reactions in which the volume of product is greater than the volume of at least one reactant. (It may be helpful to review COMMENTARY #19 at this point, to see Dalton's

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[1] Ibid. This statement appears in the Boorse and Motz reprint (op. cit.), p. 175, and Nash (op. cit.), p. 72.

COMMENTARY #22

A combination of *Coherence* truth strategy and *Pragmatic* truth strategy is operating, in the portion of Avogadro's work we have examined so far. The first theoretical statement he proposed, that equal volumes of gases should be thought to contain equal numbers of particles, required for *theoretical consistency* that he reject Dalton's theoretical model of a gas. His thinking required that he adopt the alternative model, in which particles of a gas are imagined to be separated by enormous distances, compared to the size of the particles themselves. (If this point is not obvious, you should pause now and reflect on why it is so.) *Coherence* truth strategy is operating, so far.

However, on the basis of this much theorizing, Avogadro could not account for certain *states-of-affairs information*: the observable volume ratios in the production of water from hydrogen and oxygen, for example. *Pragmatic* truth strategy demands that he change his theorizing, or else theorize further. Hence the further theoretical statement, in which he proposed the *postulated entities* we now call polyatomic molecules

We will return to our story in a moment, to see how this ingenious idea permitted Avogadro to accomplish the explanation needed. Before we do, though, a brief comment is in order. Our analysis of the truth strategies being used in particular arguments is not intended to suggest that a scientist thinks, at some point, "Aha! Now I will use X kind of truth strategy." Rather, it is to emphasize repeatedly that the truth of statements in science is established in different ways.

explanation for this peculiar phenomenon. There we used nitric oxide as our example. Because of the sequence of Avogadro's presentation, we will use water and ammonia as our first two examples here, and subsequently show how Avogadro's thinking would provide an explanation concerning nitric oxide which is an alternative to Dalton's.)

Avogadro stated that ". . . on our hypothesis, when a gas combines with two or more times its volume of another gas, the resulting compound, if gaseous, must have a volume equal to that of the first of these gases."[1] We have noticed (COMMENTARY #21) why this is so, and also that it is not the case for water: 1 volume of oxygen combines with 2 volumes of hydrogen to form 2 volumes of water (not 1). Also, it is not the case for ammonia: 1 volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia (not 1). Avogadro makes note of this problem in the case of water, and theorizes as follows: ". . . suppose that the constituent molecules [i.e., particles] of any simple gas [i.e., gaseous element] . . . are not formed of a solitary elementary molecule [i.e, atom], but are made up of a certain number of these molecules [i.e., atoms] united by attraction to form a single one."[2] (In modern terminology, such a "united molecule" of the atoms of a gaseous element would be called a polyatomic molecule. The most common examples are diatomic molecules: O_2 for oxygen, N_2 for nitrogen, etc. Here we see Avogadro suggesting these *postulated entities*, apparently for the first time in the history of chemistry.)

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #22 on page 54 (facing this page). Let us pause for a moment and examine the combination of truth strategies Avogadro was using.

Avogadro continued his argument by theorizing that the (polyatomic) constituent molecules of gaseous elements break up during a reaction, to produce "exactly what is necessary to satisfy the volume of the resulting gas." Noting that the "resulting gas" was double the volume of the reactant gas having the smaller volume, in every case he knew of, Avogadro concluded

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[1] Ibid. Boorse and Motz reprint (op. cit.), p. 177, and Nash (op. cit.), pp. 76-77.

[2] Ibid. Boorse and Motz reprint (op. cit.), p. 177, and Nash (op. cit.), p. 77.

COMMENTARY #23

In COMMENTARY #21, we pointed out that, by Avogadro's first hypothesis, the formula for ammonia would have to be NH_3, rather than NH (as proposed by Dalton). Let us write the reaction, then, based on two points. First, we have established that hydrogen is to be thought of as diatomic. Second, we note that the observed volume of product (ammonia) is twice as great as that of nitrogen; thus nitrogen is also thought to be diatomic, by Avogadro's second hypothesis.

Observed: 1 vol. N_2 + 3 vol. H_2 $\longrightarrow$ 2 vol. NH_3

Assume (for simplicity): 1 vol. N_2 particles contains 1000 N_2 molecules, hence a total of 2000 N atoms

Thus: 2000 N atoms + 6000 H atoms $\longrightarrow$ 2000 NH_3 particles

Note: 2000 ammonia particles require 2000 N atoms and 6000 H atoms, so the equation is correct as it stands, above

Equation, according to particles: $N_2 + 3H_2 \longrightarrow 2NH_3$

That example can serve as something of a check on the reasoning we used with regard to water. Let us now proceed directly to write the equation for the production of "nitrous gas" (nitric oxide), so that we can reflect on Dalton's thinking about the production of this gas. (You should now refer to COMMENTARY #19, where we examined Dalton's use of this example to refute the idea that equal volumes of gases should be thought to contain equal numbers of particles.) Since nitrogen and oxygen are both to be thought of as diatomic, the two reactants would be $N_2 + O_2$. Then, since 1 volume of nitrogen combines with 1 volume of oxygen, the formula for the product would be NO, by Avogadro's first hypothesis. Two volumes of nitric oxide are produced. Hence the equation: $N_2 + O_2 \longrightarrow 2NO$.

Here, then, is an alternative explanation to the one we developed in COMMENTARY #19, on the basis of Dalton's thinking. It is theoretically consistent, and it accounts for the observable states-of-affairs information.

that, for all such cases, "there must be a division of the [polyatomic] molecule into two [atoms]." Hence oxygen would be thought of as diatomic (O_2, by modern designation).

We can now have another look at the reaction for the production of water, and resolve a problem left at the end of COMMENTARY #21. Recall that Avogadro's first hypothesis suggested that the formula for water vapor would have to be thought to be H_2O. (If that reasoning is not clear, refer back to COMMENTARY #21.) By his second hypothesis, we see that oxygen must be thought to be O_2. Let us try to write the equation for the reaction, on that basis.

Observed: 2 vol. hydrogen + 1 vol. O_2 particles → 2 vol. H_2O particles

Assume (for simplicity): 1 vol. O_2 particles contains 1000 O_2 molecules, hence a total of 2000 O atoms

Thus: 2000 hydrogen particles + 1000 O_2 particles → 2000 H_2O particles

Question: Is hydrogen diatomic, or monatomic? (I.e., is a "particle" of hydrogen H_2, or H?)

Note: 2000 H_2O particles require 4000 H atoms

Therefore: Hydrogen must be diatomic (2000 particles X 2 atoms each)

Equation, according to particles: $2H_2 + O_2 \rightarrow 2H_2O$ (vapor)

Conveniently, but not surprisingly, the "coefficients" in the equation show the observable relationships of the volumes of gases in the reaction, while simultaneously the coefficients and the subscript numbers show the theoretical relationships among the (postulated) particles involved.

BEFORE YOU READ FURTHER . . .

- Study COMMENTARY #23 on page 56 (facing this page). Let us apply this reasoning to two other gaseous reactions.

We now consider the fourth and final point we have to resolve, in the controversy between Dalton and Gay-Lussac which we presented on pages 49-51. In the case of certain gases (ammonia was our example), the product is less dense than one of the reactants (nitrogen, in this case), even though something (hydrogen) is added to the reactant in forming the product. (Water is another example: water vapor is less dense than oxygen, even though hydrogen is added to oxygen in producing water.) Recall from COMMENTARY #20 that Dalton's thinking would permit us to resolve this problem (albeit in a complex manner), but not if we accept Avogadro's first hypothesis. Let us

COMMENTARY #24

We began this booklet with an analysis of the mole concept--the idea that a mole of theoretical particles is a standard for comparing chemical substances. The (theoretical) number of (theoretical) particles in a mole is called "Avogadro's number" (6.02×10^{23}), but the observable indicator that one has a mole of any substance is a weight: one gram-molecular weight is a mole.

What is the relationship between the story we have just completed, the events of which occurred in the early 1800's, and the modern concept of a mole? Just this. Avogadro's first hypothesis--that equal (observable) volumes of gases contain equal numbers of (theoretical) particles--is very similar in function to the mole concept of today. It provided an explanatory device for relating the observable realm to the theoretical realm, as we have seen in our story: it was a standard for comparing the observable amounts of gases reacting with each other, and for interpreting the observable comparisons in theoretical terms. The modern mole concept functions in exactly the same way, for the reactions of all substances--gases, liquids, and solids. The basic idea behind the mole concept is that identifiable "somethings" contain the same number of particles, and it was Avogadro who first demonstrated clearly how valuable this kind of thinking could be, in the interpretation of observable events in chemistry.

Avogadro's ideas, as published in 1811, were revived in 1858 by Stanislao Cannizzaro, who showed them to be of more value than competing ideas which had been developed in the intervening time.[1] During the period 1811-1858, relative atomic weights had been refined, and enough theoretical work had been done that Cannizzaro's reintroduction of Avogadro's work paved the way for its extension to liquids and solids.

One final note. By 1865, the kinetic theory of gases was sufficiently developed that an early attempt was made to calculate what we now call Avogadro's number. Josef Loschmidt, a school teacher in Vienna, calculated that one cubic centimeter of (any) gas at standard conditions (0° Celsius and 760 mm of mercury) contained 2.7×10^{19} (theoretical) particles.[2] Since it is known experimentally that one mole of (any) gas at standard conditions occupies approximately 22.4 liters, or 22,400 cubic centimeters, the number of (theoretical) particles in a mole of (any) gas should be 2.7×10^{19} times 22,400, or 6.048×10^{23}. Subsequently, calculations of Avogadro's number have been based on other theoretical work, but this early calculation by Loschmidt is rather striking.

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[1] S. Cannizzaro, "Sketch of a Course in Chemical Philosophy," reprinted in Boorse and Motz (op. cit.), pp. 282-297, from "Letter of Professor Stanislao Cannizzaro to Professor S. DeLuca," Alembic Club Reprint No. 18 (Chicago: University of Chicago Press, 1911).

[2] See A. J. Ihde, The Development of Modern Chemistry (New York: Harper & Row, 1964), p. 402, for this calculation.

try a solution to this problem on the basis of Avogadro's thinking, using ammonia as the example.

We can now write the reaction for the production of ammonia as follows: $N_2 + 3H_2 \rightarrow 2NH_3$. If we use Dalton's atomic weights (5 for N and 1 for H), we find that each "particle" of nitrogen (N_2) is to be thought to have a weight of 10, while each "particle" of ammonia (NH_3) is to be thought to have a weight of only 8. Now, if equal volumes of nitrogen and ammonia are thought to contain equal numbers of particles, the weight of a given volume of nitrogen would be greater than the weight of the same volume of ammonia. That bit of theorizing accounts for the states-of-affairs information Dalton had available at the time: that the specific gravity of nitrogen is greater than that of ammonia.

A similar line of reasoning applies to the same problem with the formation of water. (Try it. Use Dalton's atomic weight of 7, for oxygen.)

2.4. Summary: Avogadro's Ideas in Limbo for 50 Years

We have seen how very useful Avogadro's two hypotheses are, in resolving certain problems raised by the controversy between Dalton and Gay-Lussac. Avogadro's paper was published in 1811, yet his ideas did not gain widespread acceptance among chemists until after 1858. Nash demonstrates why this was so, in a fascinating account of the chemical history of that period, and the interested reader is urged to consult his work.[1] However, those considerations are not necessary for our purposes in this booklet.

NOW . . .

- Study COMMENTARY #24 on page 58 (facing this page), where we conclude our examination of the mole as an explanatory device.

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[1] Nash, op. cit., pp. 86-113.